

oxymercuration reactions.<sup>18,30</sup> Analogous rate enhancements due to neighboring group effects have also been observed by Peterson<sup>31</sup> in other electrophilic

(30) A. G. Brook, A. Rodgman, and G. F. Wright, *J. Org. Chem.*, **17**, 988 (1952); R. L. Rowland, W. L. Perry, and H. L. Friedman, *J. Am. Chem. Soc.*, **73**, 1040 (1951).

(31) P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *ibid.*, **87**, 5163 (1965).

additions (e.g., of trifluoroacetic acid) to olefins. Not unexpectedly, and in line with similar observations for other reactions,<sup>31</sup> the corresponding effect is much less marked in the oxymercuration of 1-hexen-6-ol which leads to a six-membered ring (reaction 3).

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## A Theoretical Interpretation of the Signs and Magnitudes of Some Phosphorus-31 and Silicon-29 Nuclear Spin Coupling Constants

A. H. Cowley,<sup>1a</sup> W. D. White,<sup>1b</sup> and S. L. Manatt<sup>1c</sup>

*Contribution from the Department of Chemistry, University of Texas, Austin, Texas 78712, and the Space Sciences Division, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91103.*

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**Abstract:** An attempt has been made to explain the observed pattern of signs and magnitudes of the <sup>31</sup>P-<sup>1</sup>H, <sup>31</sup>P-<sup>19</sup>F, <sup>31</sup>P-<sup>31</sup>P, <sup>29</sup>Si-<sup>1</sup>H, and <sup>29</sup>Si-<sup>19</sup>F nuclear spin coupling constants on the basis of the Pople and Santry expression for the contact term. To do this it was necessary to perform LCAO-MO calculations on the following model compounds: PH<sub>3</sub>, PH<sub>4</sub><sup>+</sup>, PF<sub>3</sub>, P<sub>2</sub>, SiH<sub>4</sub>, and SiF<sub>4</sub>. Both extended Hückel and self-consistent field calculations were employed. With the exception of SiF<sub>4</sub>, a satisfactory agreement between the observed and calculated signs was observed. The calculated magnitudes of the coupling constants also correlate with the observed values but are lower by a factor of between 2 and 3.

Recently we have had occasion to determine the relative signs and magnitudes of the nuclear spin coupling constants in a number of compounds involving directly bonded P-H, P-F, and P-P linkages.<sup>2</sup> In this study it was shown that the signs of the <sup>31</sup>P-<sup>1</sup>H, <sup>31</sup>P-<sup>19</sup>F, and <sup>31</sup>P-<sup>31</sup>P coupling constants are positive, negative, and negative, respectively. Earlier Danyluk had demonstrated that the <sup>29</sup>Si-<sup>1</sup>H and <sup>29</sup>Si-<sup>19</sup>F coupling constants are opposite in sign.<sup>3</sup> In the present paper we attempt to gain a theoretical understanding of the pattern of signs and magnitudes which has been observed for the above couplings.

The interactions which lead to spin-spin coupling in liquids were first formulated by Ramsey<sup>4</sup> in terms of a contact (Fermi) mechanism, a spin-orbital mechanism, and a spin-polarization mechanism. Later McConnell<sup>5</sup> showed that Ramsey's formulas could be applied to large molecules if LCAO molecular orbitals were used in conjunction with the "average excitation energy" approximation. By the latter one means that all triplet states interacting with the ground state are replaced

by a suitable average value. This approach, which also eliminates triplet-state wave functions, produced useful formulas for calculating various coupling constants, but necessarily could predict only positive signs. The next significant step was taken by Pople and Santry<sup>6</sup> who avoided the use of the "average excitation energy" approximation and were thus able to predict a satisfactory pattern for the signs and magnitudes of the coupling constants between various directly bonded atoms up to fluorine.

In the present paper we extend the Pople and Santry approach to various couplings involving phosphorus and silicon. The majority of the experimental results are discussed in relation to the contact term. However, we have attempted to estimate the orbital and spin-dipolar contributions in those couplings which do not involve hydrogen.

The molecular orbital expression for the contact contribution to the spin-spin coupling constant between directly bonded nuclei A and B is given by<sup>6</sup>

$$J_{AB} = \frac{-64}{9} \beta^2 \gamma_A \gamma_B h \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (\delta^3 \Delta E_{i \rightarrow j})^{-1} \times (\psi_i | \delta(r_A) | \psi_j) (\psi_j | \delta(r_B) | \psi_i) \quad (1)$$

where  $\beta$  is the Bohr magneton,  $\gamma$  is the magnetogyric ratio, and the terms in the summation relate to the interaction of the triplet excited states with the ground state evaluated at the A and B nuclei. In the LCAO

(1) (a) University of Texas; (b) Union Carbide Predoctoral Fellow, University of Texas; (c) Jet Propulsion Laboratory.

(2) S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, *J. Am. Chem. Soc.*, **89**, 4544 (1967).

(3) S. S. Danyluk, *ibid.*, **86**, 4504 (1964). This author found that  $J_{\text{Si-F}}$  is positive and  $J_{\text{Si-H}}$  is negative. However, if one employs the "reduced coupling constant," which is defined as  $K_{AB} = (2\pi/\hbar\gamma_A\gamma_B)J_{AB}$ , the signs of these couplings are reversed. Thus  $K_{\text{Si-H}}$  and  $K_{\text{P-H}}$  are positive, and  $K_{\text{P-F}}$ ,  $K_{\text{Si-F}}$ , and  $K_{\text{P-P}}$  are negative.

(4) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953). In the liquid phase the direct dipolar interactions, which lead to line broadening in solids, average to zero owing to rapid rotation.

(5) H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

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

approximation eq 1 becomes

$$J_{AB} = \frac{-64}{9} \beta^2 \gamma_A \gamma_B h \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (\Delta E_{i \rightarrow j})^{-1} \times \sum_{\lambda \mu \nu \sigma} C_{i\lambda} C_{j\mu} C_{j\nu} C_{i\sigma} (\phi_\lambda | \delta(r_A) | \phi_\mu) (\phi_\nu | \delta(r_B) | \phi_\sigma) \quad (2)$$

If only one-center integrals involving valence s orbitals on atoms A or B are retained, *i.e.*,  $\phi_\lambda$  and  $\phi_\mu$  are valence s orbitals on A ( $S_A$ ) and  $\phi_\nu$  and  $\phi_\sigma$  are valence s orbitals on B ( $S_B$ ), then

$$J_{AB} = \frac{-64}{9} \beta^2 \gamma_A \gamma_B h (S_A | \delta(r_A) | S_A) (S_B | \delta(r_B) | S_B) \times \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (\Delta E_{i \rightarrow j})^{-1} C_{iS_A} C_{jS_A} C_{jS_B} C_{iS_B} \quad (3)$$

In the one-electron MO approximation eq 3 becomes

$$J_{AB} = \frac{64}{9} \beta^2 \gamma_A \gamma_B h (S_A | \delta(r_A) | S_A) (S_B | \delta(r_B) | S_B) \times \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (\epsilon_i - \epsilon_j)^{-1} C_{iS_A} C_{jS_A} C_{jS_B} C_{iS_B} \quad (4)$$

Since calculation of the coupling constants by either eq 3 or eq 4 requires a knowledge of LCAO coefficients and molecular orbital energies, it was first necessary to perform such calculations. The selection of  $\text{PH}_3$ ,  $\text{PH}_4^+$ ,  $\text{PF}_3$ ,  $\text{P}_2$ ,  $\text{SiH}_4$ , and  $\text{SiF}_4$  as model compounds is based on the fact that they represent the simplest symmetrical molecules involving the linkages of interest. Molecular orbital calculations have been published previously<sup>7</sup> for  $\text{PH}_3$ ,  $\text{PH}_4^+$ , and  $\text{SiH}_4$ . However, since these calculations were not of the LCAO type they were inappropriate for the present argument. While our work was in progress Boyd and Lipscomb<sup>8</sup> published some LCAO-SCF calculations on  $\text{PH}_3$ ,  $\text{PO}$ ,  $\text{PO}^-$ , and  $\text{P}_2$ .

## Methods and Results

Two types of molecular orbital calculation were employed. All calculations were performed on the CDC 6600 computer at the University of Texas Computation Center.

(a) **Extended Hückel Calculations.** One-electron wave functions and energies were computed using the program developed by Hoffmann.<sup>9</sup> Slater atomic orbitals with exponents of 1.1 for hydrogen, 1.383 for silicon, 1.6 for phosphorus, and 2.6 for fluorine were used as a basis set. The atomic coordinates were calculated from the pertinent bond distances and bond angles.<sup>10</sup> The following valence-state ionization potentials (vsip)<sup>11</sup> were used for the diagonal element of the H matrix (ev):  $H_{\mu\mu} = -13.6$  (H 1s),  $-38.24$  (F 2s),  $-20.86$  (F 2p),  $-17.31$  (Si 3s),  $-9.19$  (Si 3p),  $-20.20$  (P 3s), and  $-12.49$  (P 3p). The off-diagonal elements were evaluated by the Wolfsberg-Helmholtz approximation<sup>12</sup>

$$H_{\mu\nu} = 0.5K(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu} \quad (5)$$

with  $K = 1.75$ .

(7) R. Moccia, *J. Chem. Phys.*, **40**, 2164, 2176 (1964).

(8) D. B. Boyd and W. N. Lipscomb, *ibid.*, **46**, 910 (1967).

(9) R. Hoffmann, *ibid.*, **39**, 1397 (1963), and references therein. The authors are grateful to Professor Hoffmann for a copy of his program.

(10) Data taken from "Tables of Interatomic Distances and Configurations in Molecules and Ions," L. E. Sutton, Ed., Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965.

(11) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(12) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

(b) **Self-Consistent Field Calculations.** These calculations were performed using a program written in our laboratories by one of the authors (W. D. W.) and M. W. Taylor. The program is based on the approximate SCF-MO theory of Pople, Santry, and Segal,<sup>13</sup> in which differential overlap is neglected. The first part of the procedure involves calculating an initial set of molecular orbital coefficients,  $C_{i\mu}$ , by an extended Hückel procedure in which the diagonal elements of the  $H$  matrix are replaced by the "average" ionization potentials and the off-diagonal elements by  $\beta^0 S_{\mu\nu}$ . The following "average" ionization potentials were used (ev):<sup>13</sup>  $-13.06$  (H 1s),  $-40.20$  (F 2s), and  $-18.66$  (F 2p). In the cases of P and Si we used the vsip values<sup>11</sup> (*vide supra*). The bonding parameter values of  $\beta^0(\text{H}) = -9.0$  ev and  $\beta^0(\text{F}) = -39.0$  ev were taken from ref 13. We used a value of  $\beta^0(\text{P}) = -20.0$  ev on the basis of the best over-all fit of our calculations for  $\text{PO}^-$  with the more accurate LCAO-SCF calculations of Boyd and Lipscomb.<sup>8</sup> For silicon the value  $\beta^0(\text{Si}) = -17.0$  ev was employed. The overlap integrals,  $S_{\mu\nu}$ , were calculated using the formulas of Mulliken, Rieke, Orloff, and Orloff.<sup>14</sup>

The next stage involves calculation of the charge density and bond-order matrix

$$P_{\mu\nu} = 2 \sum_i^{\text{occ}} C_{i\mu} C_{i\nu} \quad (6)$$

The  $P_{\mu\nu}$  matrix is then used to form a Hartree-Fock matrix,  $F_{\mu\nu}$ , which is solved to give a new set of molecular orbital coefficients,  $C_{i\mu}$ . This procedure is repeated until self-consistency is reached with a tolerance of 0.001 on all  $C_{i\mu}$ . Output of the program includes the molecular orbital coefficients,  $C_{i\mu}$ , the corresponding eigenvalues,  $E_i$ , the charge density and bond-order matrix,  $P_{\mu\nu}$ , and a Mulliken overlap population analysis.<sup>15</sup>

The molecular orbital coefficients of the valence s atomic orbitals ( $C_{iS_A}$ , etc.) and the corresponding eigenvalues for  $\text{PH}_3$ ,  $\text{PF}_3$ ,  $\text{PH}_4^+$ ,  $\text{P}_2$ ,  $\text{SiH}_4$ , and  $\text{SiF}_4$  are shown in Tables I-V. Only those molecular orbitals which involve the Si 3s and P 3s atomic orbitals are included. In the  $T_d$  and  $C_{3v}$  species these are  $A_1$ -type molecular orbitals. In  $\text{P}_2$  they are  $\sigma$ -type molecular orbitals. Three calculations of each coupling constant of interest were then performed by substituting the two sets of extended Hückel data (with and without differential overlap) in eq 4 and the SCF data in eq 3.

Also necessary for such calculations are the magnetogyric ratios and the magnitudes of the valence s atomic orbitals at the nuclei (Table III). The latter are taken from the data of Morton, Rowlands, and Whiffen<sup>16</sup> except for hydrogen where a Slater orbital with  $Z = 1.2$  was used.<sup>6</sup>

The portion of eq 3 and 4 which is responsible for the variation in the signs of the coupling constants is  $\pi_{AB}$ , a term analogous to the "mutual polarizability"

(13) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965).

(14) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *ibid.*, **17**, 1248 (1949).

(15) R. S. Mulliken, *ibid.*, **23**, 1833, 1841, 2338, 2343 (1955).

(16) J. R. Morton, J. R. Rowlands, and D. H. Whiffen, National Physical Laboratory Report, BPR 13, 1962.

Table I. Valence s Atomic Orbital Coefficients and Eigenvalues of Phosphorus Compounds

EHMO			EHMO with CNDO			SCF			Single-triplet excitation energy, ev
LCAO coefficients		Energy, ev	LCAO coefficients		Energy, ev	LCAO coefficients		Orbital no.	
PH <sub>3</sub>									
P 3s	H 1s		P 3s	H 1s		P 3s	H 1s		
-1.470	0.891	37.402	-0.485	0.411	-2.668	-0.485	0.411	3	
0.336	-0.102	-13.362	0.509	-0.140	-14.535	0.464	-0.163	2	<sup>3</sup> ΔE <sub>2→3</sub> = 11.691
0.674	0.202	-22.850	0.711	0.381	-31.247	0.742	0.371	1	<sup>3</sup> ΔE <sub>1→3</sub> = 27.181
PH <sub>4</sub> <sup>+</sup>									
P 3s	H 1s		P 3s	H 1s		P 3s	H 1s		
1.651	-0.750	35.703	-0.651	0.378	-4.119	-0.607	0.395	2	
0.644	0.173	-23.197	0.759	0.326	-32.033	0.795	0.304	1	<sup>3</sup> ΔE <sub>1→2</sub> = 27.458
PF <sub>3</sub>									
P 3s	F 2s		P 3s	F 2s		P 3s	F 2s		
-1.009	0.471	11.255	-0.471	0.180	-3.159	0.481	-0.212	5	
-0.563	0.067	-13.310	0.584	-0.070	-12.170	0.337	-0.025	4	<sup>3</sup> ΔE <sub>4→5</sub> = 9.537
-0.068	-0.022	-19.116	0.315	-0.007	-22.203	-0.270	0.197	3	<sup>3</sup> ΔE <sub>3→5</sub> = 19.466
-0.335	0.129	-20.161	-0.378	0.231	-23.799	0.597	-0.128	2	<sup>3</sup> ΔE <sub>2→5</sub> = 19.955
0.210	0.503	-41.795	0.441	0.493	-50.064	0.473	0.487	1	<sup>3</sup> ΔE <sub>1→5</sub> = 45.117
P <sub>2</sub>									
P(1) 3s	P(2) 3s		P(1) 3s	P(2) 3s		P(1) 3s	P(2) 3s		
0.775	-0.775	9.394	0.336	-0.336	-1.490	0.336	-0.336	4	
-0.245	-0.245	-13.491	0.381	0.381	-15.380	-0.287	-0.287	3	<sup>3</sup> ΔE <sub>3→4</sub> = 12.493
0.606	-0.606	-17.207	-0.622	0.622	-17.966	0.622	-0.622	2	<sup>3</sup> ΔE <sub>2→4</sub> = 16.476
0.594	0.594	-23.843	0.596	0.596	-30.544	0.646	0.646	1	<sup>3</sup> ΔE <sub>1→4</sub> = 25.804

Table II. Valence s Atomic Orbital Coefficients and Eigenvalues of Silicon Compounds

EHMO			EHMO with CNDO			SCF			Singlet-triplet excitation energy, ev
LCAO coefficients		Energy, ev	LCAO coefficients		Energy, ev	LCAO coefficients		Orbital no.	
SiH <sub>4</sub>									
Si 3s	H 1s		Si 3s	H 1s		Si 3s	H 1s		
-1.782	0.803	40.214	-0.682	0.365	-3.944	-0.671	0.370	2	
0.580	0.204	-21.015	0.731	0.341	-28.927	0.742	0.336	1	<sup>3</sup> ΔE <sub>1→2</sub> = 24.216
SiF <sub>4</sub>									
Si 3s	F 2s		Si 3s	F 2s		Si 3s	F 2s		
1.252	-0.412	9.211	0.812	-0.181	-5.874	0.835	-0.180	3	
0.173	-0.079	-19.414	-0.351	0.161	-22.186	-0.341	0.130	2	<sup>3</sup> ΔE <sub>2→3</sub> = 18.887
0.183	0.441	-41.512	0.467	0.437	-49.092	0.431	0.449	1	<sup>3</sup> ΔE <sub>1→3</sub> = 44.200

Table III. Magnitudes of Valences Atomic Orbitals at the Nuclei

Nucleus	(S δ(r) S)
<sup>1</sup> H	0.55
<sup>19</sup> F	11.397
<sup>29</sup> Si	3.807
<sup>31</sup> P	5.625

Table IV. Calculated and Experimental Coupling Constants

Mole- cule	Calculated J, cps			Exptl magnitude	Exptl sign <sup>a</sup>
	EHMO	EHMO with CNDO	SCF		
PH <sub>3</sub>	+189.39	+63.19	+66.55	182.2 <sup>b</sup>	+
PH <sub>4</sub> <sup>+</sup>	+213.74	+199.05	+192.58	...	+
PF <sub>3</sub>	-736.15	-640.66	-424.43	1441 <sup>d</sup>	-
P <sub>2</sub>	-128.95	-34.33	-30.54	...	-
SiH <sub>4</sub>	-83.80	-75.27	-77.47	202.5 <sup>f</sup>	-
SiF <sub>4</sub>	-339.38	-109.21	-180.37	178 <sup>d</sup>	+

<sup>a</sup> These signs are based on sign determinations in other molecules. See ref 2 and 3. <sup>b</sup> R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961). <sup>c</sup> No information is available concerning PH<sub>4</sub><sup>+</sup>. However, in (CH<sub>3</sub>)<sub>3</sub><sup>+</sup>PH J<sub>PH</sub> = 515 cps. B. Silver and Z. Luz, *J. Am. Chem. Soc.*, **83**, 786 (1961). <sup>d</sup> E. L. Muettterties and W. D. Phillips, *ibid.*, **81**, 1084 (1959). <sup>e</sup> See Table V for a summary of J<sub>P-P</sub> values. <sup>f</sup> E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, **36**, 2628 (1962).

Table V. Summary of J<sub>P-P</sub> Values (cps)

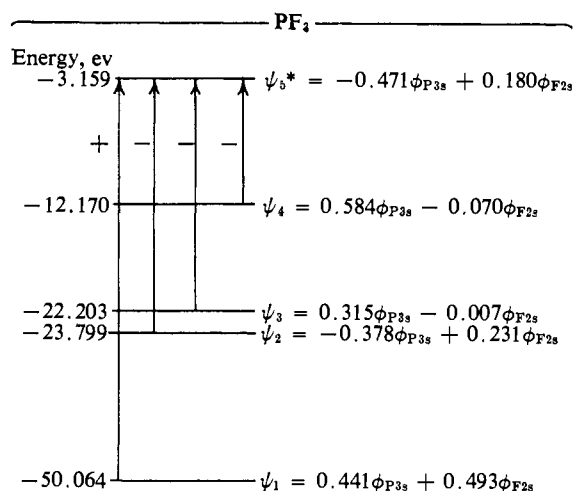
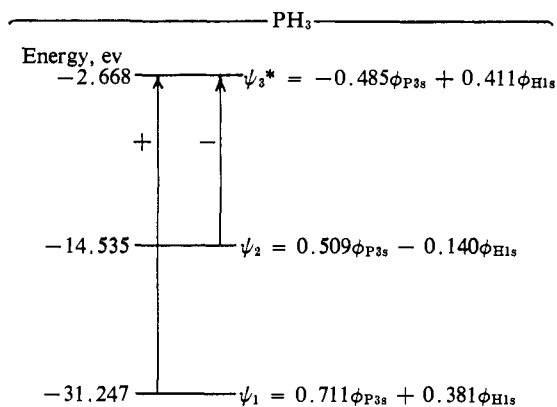
H <sub>2</sub> P-PH <sub>2</sub>	108.2  <sup>a</sup>
(CH <sub>3</sub> ) <sub>2</sub> P-P(CH <sub>3</sub> ) <sub>2</sub>	-179.6 <sup>b</sup>
S    (CH <sub>3</sub> ) <sub>2</sub> P-P(CH <sub>3</sub> ) <sub>2</sub>	220  <sup>c</sup>
(CH <sub>3</sub> ) <sub>2</sub> P-P(CF <sub>3</sub> ) <sub>2</sub>	-256 <sup>d</sup>
(CH <sub>3</sub> ) <sub>3</sub> P <sup>+</sup> -PCF <sub>3</sub> <sup>-</sup>	-443 <sup>d</sup>
[O O]       O-P-P-H       O O	480  <sup>e</sup>

<sup>a</sup> R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961). <sup>b</sup> R. K. Harris, private communication. <sup>c</sup> R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964). <sup>d</sup> S. L. Manatt, A. H. Cowley, and A. B. Burg, to be published. <sup>e</sup> C. F. Callis, J. R. Van Wazer, J. N. Shoolery, and W. A. Anderson, *J. Am. Chem. Soc.*, **79**, 2719 (1957).

of atoms A and B<sup>17</sup>

$$\pi_{AB} = 4 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (\epsilon_i - \epsilon_j)^{-1} C_{iSA} C_{jSA} C_{jSB} C_{iSB} \quad (7)$$

(17) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947).



Using the extended Hückel data (with complete neglect of differential overlap) we next exemplify how the directly bonded couplings in  $\text{PH}_3$  and  $\text{PF}_3$  depend on the excitations from the occupied to unoccupied orbitals. In Figure 1 it can be seen that two such excitations are possible in  $\text{PH}_3$ , hence the summation in eq 7 involves two terms. The positive contribution from the  $\psi_1 \rightarrow \psi_3$  excitation is larger than the negative contribution from the  $\psi_2 \rightarrow \psi_3$  excitation resulting in a positive value for  $\pi_{\text{PH}}$  and  $J_{\text{PH}}$ . In  $\text{PF}_3$  the positive contribution from the  $\psi_1 \rightarrow \psi_5$  excitation is offset by the negative contributions from the  $\psi_2 \rightarrow \psi_5$ ,  $\psi_3 \rightarrow \psi_5$ , and  $\psi_4 \rightarrow \psi_5$  excitations resulting in a substantial negative value for  $\pi_{\text{PF}}$  and  $J_{\text{PF}}$ .

## Discussion

With the exception of  $\text{SiF}_4$  the molecular orbital approach gives satisfactory predictions for the signs of the various directly bonded coupling constants involving  $^{31}\text{P}$  and  $^{29}\text{Si}$  (Table IV). Initially it was felt that the problem with  $\text{SiF}_4$  might be due to substantial contributions from the orbital and spin dipolar coupling mechanisms since these contributions are nonzero when neither of the directly bonded nuclei is hydrogen. However, using the Pople and Santry expressions for these mechanisms<sup>6</sup> we estimate that in  $\text{SiF}_4$   $J(\text{orbital}) = +18.2$  cps, and  $J(\text{spin dipolar}) = -1.2$  cps, hence the overall noncontact contribution of +17.0 cps is insufficient to alter the sign of the  $^{29}\text{Si}-^{19}\text{F}$  coupling constant.

From the standpoint of the contact term the difficulty with  $\text{SiF}_4$  arises because the positive contribution from the lowest occupied to unoccupied excitation ( $\psi_1 \rightarrow \psi_3$ ) is larger than the negative contribution from the other occupied to unoccupied excitation ( $\psi_2 \rightarrow \psi_3$ ). The situation could thus be remedied by (a) raising the energy of  $\psi_2$ ; (b) increasing the magnitudes of the valence s atomic orbital coefficient in  $\psi_2$ ; (c) lowering the energy of  $\psi_1$ ; or (d) decreasing the magnitudes of the valence s atomic orbital coefficients in  $\psi_1$ .

In view of the difficulties with  $\text{SiF}_4$ , it was considered important to see whether the molecular orbital approach used here was capable of predicting the observed<sup>18</sup> dif-

(18) G. V. D. Tiers, *J. Am. Chem. Soc.*, **84**, 3972 (1962), found that  $J^{13}\text{C}-^{19}\text{F}$  is negative relative to  $J^{13}\text{C}-^1\text{H}$ .

ference in sign between  $J^{13}\text{C}-^1\text{H}$  and  $J^{13}\text{C}-^{19}\text{F}$  using  $\text{CH}_4$  and  $\text{CF}_4$  as model compounds. The extended Hückel, extended Hückel with complete neglect of differential overlap, and SCF calculations gave  $J^{13}\text{C}-^1\text{H} = +58.8$ ,<sup>19</sup> +53.5, and +55.1 cps, respectively, for  $\text{CH}_4$ , and  $J^{13}\text{C}-^{19}\text{F} = +162$ , +10, and -40.5 cps, respectively, for  $\text{CF}_4$ . These compare with the experimental values of  $J^{13}\text{C}-^1\text{H} = +125$  cps for  $\text{CH}_4$ <sup>20</sup> and  $J^{13}\text{C}-^{19}\text{F} = -257$  cps in  $\text{CF}_4$ .<sup>21</sup> It is apparent that the extended Hückel calculations of the  $^{29}\text{Si}-^{19}\text{F}$  and  $^{13}\text{C}-^{19}\text{F}$  couplings show the same trend, namely an improvement in results when differential overlap is neglected. However, with  $\text{CF}_4$  the SCF calculation is able to yield the correct sign for  $J^{13}\text{C}-^{19}\text{F}$ .

In general the magnitudes of the coupling constants as calculated on the basis of the contact term reproduce the trends of the experimental values but are too small by a factor of between 2 and 3. Of the three types of calculation attempted, the Hoffmann extended Hückel method is generally the most satisfactory, hence the inclusion of overlap appears to be important.

The discrepancy between the calculated and experimental coupling constants is apparently not caused by neglect of the orbital and spin dipolar terms, since these are zero if one of the directly bonded nuclei is hydrogen (*i.e.*, in  $\text{PH}_3$ ,  $\text{PH}_4^+$ , and  $\text{SiH}_4$ ) and small in relation to the experimental values in  $\text{PF}_3$  and  $\text{SiF}_4$  (Table IV). Silicon tetrafluoride has been discussed above, and in  $\text{PF}_3$  the orbital and spin dipolar terms are estimated to be -103.0 and +13.8 cps, respectively. However, the estimated orbital and spin dipolar contributions of -55.5 and +21.5 cps in  $\text{P}_2$  represent a more substantial fraction of the observed  $^{31}\text{P}-^{31}\text{P}$  coupling constants (Table V). This is not too surprising in view of the  $\pi$  bonding in the  $\text{P}_2$  molecule.<sup>8</sup>

Further progress in the calculation of signs and magnitudes of coupling constants will probably come from improvements in the molecular orbital energies and LCAO coefficients. One approach which shows some

(19) R. C. Fahey, G. C. Graham, and R. L. Piccioni, *J. Am. Chem. Soc.*, **88**, 193 (1966), have shown that this value can be increased to 83 cps if terms involving products of one- and two-center integrals are included in the extended Hückel calculation.

(20) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).

(21) N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963).

promise in this regard is the semiempirical SCF-MO method developed by Dewar and Klopman.<sup>22</sup> Use of these authors' eigenvector and eigenvalue data for CH<sub>4</sub> yields a value of +80.1 cps in this molecule. This compares with the extended Hückel value of +58.0 cps.

The calculations with PH<sub>3</sub> and PH<sub>4</sub><sup>+</sup> indicate that the <sup>31</sup>P-<sup>1</sup>H coupling constant increases on going from a phosphine to a phosphonium cation. If the <sup>31</sup>P-<sup>1</sup>H coupling constant of PH<sub>4</sub><sup>+</sup> is low by the same factor as that of PH<sub>3</sub> then  $J_{PH}$  of the phosphonium cation should be 562 cps (according to the extended Hückel with CNDO calculations), which is in fair agreement with the experimental value of 515 cps for the trimethylphosphonium cation.<sup>23</sup> The increase of  $J_{PH}$  on quaternization suggests the possibility of a linear relationship of this coupling constant with the s character of the bonding orbitals. However, it has been shown previously<sup>24</sup> that no such simple correlation exists.

(22) M. J. S. Dewar and G. Klopman, *J. Am. Chem. Soc.*, **89**, 3089 (1967).

(23) B. Silver and Z. Luz, *ibid.*, **83**, 786 (1961).

(24) S. L. Manatt, G. L. Juvinal, R. I. Wagner, and D. D. Elleman, *ibid.*, **88**, 2689 (1966).

Very recently it has been demonstrated<sup>25</sup> that the <sup>13</sup>C-<sup>13</sup>C coupling constant is positive. By contrast the <sup>31</sup>P-<sup>31</sup>P coupling constant is negative (the available data are shown in Table V). It may be that homonuclear directly bonded coupling constants of the third row are all negative. For this reason it would be interesting to know the sign of the <sup>29</sup>Si-<sup>29</sup>Si coupling constant. The hybridizational and inductive effects on the <sup>31</sup>P-<sup>31</sup>P coupling constant are not yet clear. The only obvious trend in the data in Table V is that the magnitude of  $J_{PP}$  increases when phosphorus is oxidized.

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(25) D. M. Grant, *ibid.*, **89**, 2228 (1967).

## Vibrational Spectra and Rotational Isomerism in Acrylyl Fluoride

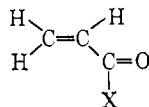
Gerald L. Carlson, William G. Fateley, and Robert E. Witkowski

Contribution from the Mellon Institute, Pittsburgh, Pennsylvania 15213.

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**Abstract:** A temperature-dependence study of the infrared spectrum of acrylyl fluoride has been carried out to obtain information on the rotational isomerism previously reported for this molecule. This study shows that, if a rotational equilibrium does exist, there is very little difference between the spectra of the two forms and the energy difference between the two forms is very small. The complete infrared and Raman spectra and their assignment on the basis of C<sub>s</sub> symmetry are also reported. The torsional frequency about the C-C single bond was observed at 115 cm<sup>-1</sup>, giving a barrier to internal rotation ( $V^*$ ) of 18.6 kcal/mole.

There have been a number of recent papers concerning rotational isomerism<sup>1,2</sup> and torsional frequencies<sup>3,4</sup> in butadiene- and acrolein-type molecules. Of particular interest have been the acrylyl halides



In the case of the fluoride, Koster<sup>1</sup> has shown by nmr methods that the molecule exists as an equilibrium mixture of an *s-trans* and an *s-cis* (or skew) form with an energy difference of 800 ± 250 cal/mole. Infrared studies on the chloride and bromide by Katon and Fearheller<sup>2</sup> have yielded similar results. These workers found that both acrylyl chloride and bromide exist in two forms and that the energy difference for the chloride was about 600 cal/mole.

(1) D. F. Koster, *J. Am. Chem. Soc.*, **88**, 5067 (1966), and references cited therein.

(2) J. E. Katon and W. R. Fearheller, Jr., *J. Chem. Phys.*, in press.

(3) R. K. Harris and R. E. Witkowski, *Spectrochim. Acta*, **20**, 1651 (1964).

(4) W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *ibid.*, **21**, 231 (1965).

Our interest in acrylyl fluoride was twofold. One difficulty in the calculation of potential barriers about the C-C single bond in conjugated molecules has been the lack of sufficient data to evaluate the relative magnitude of the various terms in the potential function.<sup>4</sup> This problem can be solved for a molecule which exists as an equilibrium mixture of two forms if the torsional frequency for each form and the energy difference between the two forms can be obtained. The acrylyl fluoride molecule appeared to be a promising case for obtaining these data. Secondly, we have recently described an improved method for the calculation of equilibrium constants from infrared data<sup>5</sup> and were interested in testing the method on additional molecules.

In this paper we are reporting on the results of an infrared investigation of the rotational equilibrium in acrylyl fluoride. Also included are the complete infrared and Raman spectra, an assignment of the fundamental vibrational frequencies, and the calculation of the barrier to internal rotation about the C-C single bond.

(5) K. O. Hartman, G. L. Carlson, W. G. Fateley, and R. E. Witkowski, *ibid.*, in press.