^{13}C Nuclear Magnetic Resonance of Organophosphorus Compounds. I. Diethyl Phosphonates

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Abstract: A series of organophosphorus compounds, $(C_2H_5O)_2P(O)CH_2X$, has been examined using high-resolution ^{13}C nmr for X = OCH_3, I, Cl, H, CN, $CH(OC_2H_5)_2$, p-NH_2Ph, $CHCH_2$, C_6H_5, CH_2Br, $CONH_2$, CH_3, $CO_2C_2H_5$, and CHO. ^{13}C chemical shifts of the ethoxy carbons were insensitive to X while the phosphonate carbon varied over 79 ppm. Similarly, the couplings of the ethoxy carbons to the phosphorus were essentially constant, clustering around +5.7 Hz for $^2J_{CP}$ and −6.4 Hz for $^3J_{CP}$, while the directly bonded $^1J_{CP}$ decreased from +163.9 Hz for X = OCH_3 in the above order to +126.5 Hz for X = CHO, a range of almost 30%. The data are discussed in terms of the various theoretical models previously used for spin couplings and chemical shifts. Changes in effective nuclear charge do not appear to be the controlling factor in changes of carbon-phosphorus couplings in these compounds. Approximate SCF-MO methods are more successful in reproducing the experimental results. There is a linear relationship between $P^2_{s_C s_P}$ and $^1J_{CP}$ in these compounds, although the coupling constant changes almost twice as fast as the bond order.

The multifaceted nature of the chemistry of phosphorus has provided both interest and challenge to chemists, not only in terms of an understanding of the reactions in which it participates, but also in better comprehending the bonding which bestows this complex chemistry. High-resolution nuclear magnetic resonance has been employed liberally in pursuit of these aims, with primarily ^{1}H and ^{31}P serving as the nuclear probes. The ^{13}C nucleus has been much less utilized in this regard in large part due to the low natural abundance (1.1%) and low magnetogyric ratio (one-fourth that of the proton). In principal, information gained from ^{13}C nmr studies on compounds containing phosphorus can certainly complement and most likely have greater value than that from direct ^{31}P or ^{1}H high-resolution nmr. The validity of this statement rests on several facts. First the large majority of interesting phosphorus-containing materials are organophosphorus compounds of both synthetic and natural origin. The carbon atoms in these molecules serve as indicators of molecular electronic structure through their high-resolution nmr parameters. The protons participate in the molecular binding to a much smaller extent. The phosphorus atom, while contributing to the specific chemistry of the organophosphorus compound, gives only one chemical shift parameter, while the couplings to ^{1}H and ^{13}C can be much more easily extracted from their respective spectra. Secondly, according to Ramsey's[1] formulation of chemical shift theory, the shielding experienced by a nucleus can be considered to arise from two major contributions, the diamagnetic and paramagnetic shieldings. For protons these are of nearly equal size while opposite in sign. This gives rise to the narrow range of proton shifts and concomitant theoretical difficulty in accurately reproducing a difference between two large but oppositely signed contributions. This problem is minimized as heavier atoms are considered. In these cases changes in the paramagnetic contribution are mainly responsible for the range of chemical shift and offer greater hope of theoretical prediction. As the atomic number increases, however, d orbitals become more involved in bonding, particularly as the transition series is encountered. Phosphorus lies in the mid region where the importance and contribution of d orbitals are variable and poorly understood quantitatively. This factor makes ^{31}P shifts more difficult to interpret than those of lighter atoms. These factors, coupled with the known range and sensitivity of ^{13}C chemical shifts, make the studying of organophosphorus compounds using ^{13}C nmr certainly promising.

Mainly for instrumental reasons the use of ^{13}C nmr has been, until recently, restricted to a small number of laboratories. This situation is changing quickly, however. The bulk of previous ^{13}C nmr in organophosphorus compounds has been done in the last 3 years and has centered on ^{13}C–^{31}P nuclear spin coupling. The first determination of ^{13}C–^{31}P coupling constants was performed by McFarlane[2] in dimethylphenylphosphine (−14 ± 1 Hz) and its corresponding hydrogen phosphonium salt (+56 ± 1 Hz). Using the same heteronuclear "tickling" techniques, McFarlane[3] determined the two-bond ^{13}C–O–^{31}P coupling in $(CH_3O)_2P(O)H$ as −6.0 ± 1 Hz. Finer and Harris[4] were able to get an approximate value of 14 Hz for directly bonded ^{13}C–^{31}P coupling in $(CH_3)_2P$–$P(CH_3)_2$. In a larger study of 22 organophosphorus compounds, including phosphines, phosphine oxides, sulfides and selenides, phosphonium salts, and phosphonates, McFarlane has made general comments regarding the sign dependence of one-, two-, and three-bond couplings on the valency of the phosphorus atom,[5] tabulated ^{13}C chemical shifts,[5] and determined ^{13}C–^{31}P coupling data in a polycyclic system[6] and phosphorus–selenium compounds.[7]

Mavel and Green[8] have reported further ^{13}C shift and ^{13}C–^{31}P coupling data in CH_3PCl_2, $CH_3P(S)Cl_2$, $CH_3P(O)Cl_2$, and $CH_3P(O)F_2$. With the aid of heteronuclear double resonance, Elser and Dreeskamp[9]

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(1) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); **86**, 243 (1952).

(2) W. McFarlane, *Chem. Commun.*, 58 (1967).

(3) W. McFarlane, *J. Chem. Soc. A*, 1148 (1967).

(4) E. G. Finer and R. K. Harris, *Mol. Phys.*, **13**, 65 (1967).

(5) W. McFarlane, *Proc. Roy. Soc., Ser. A*, **306**, 185 (1968).

(6) W. McFarlane and J. A. Nash, *Chem. Commun.*, 127 (1969).

(7) W. McFarlane and J. A. Nash, *ibid.*, 913 (1969).

(8) G. Mavel and M. J. Green, *ibid.*, 742 (1968).

evaluated ^{13}C–^{31}P couplings in $P(CH_3)_3$, $P(CH_3)_4^+$, and model compounds $(C_6H_5)_2PX(CH_3)_3$, X = C, Si, Sn. Carbon–phosphorus couplings were recently reported in $(C_6H_5)_3P$, $(C_4H_7)_3P^+$ by Weigert and Roberts[10] using high-resolution ^{13}C nmr. Two-bond ^{13}C–^{31}P coupling in $P(OCH_3)_3$ and molybdenum carbonyl complexes with $P(OCH_3)_3$ were determined by Bertrand, Ogilvie, and Verkade,[11] who subsequently reported the one- and two-bond ^{13}C–^{31}P couplings in $[CH_3P(OCH_3)_3]^+BF_4^-$ (+132.4 and −6.8 Hz, respectively[12]) and the two-bond couplings of the type ^{31}P–N–^{13}C in $P[N(CH_3)_2]_3$ and $OP[N(CH_3)_2]_3$.

There have been few attempts at theoretically reproducing ^{13}C–^{31}P coupling constants. This is, in part, due to the primitive state of spin coupling theory and difficulties in finding accurate molecular wave functions, but mainly is due to the until recent paucity of experimental data. As part of a general theoretical treatment of spin coupling, Cowley and White[13] used a parameterized LCAO–SCF–MO theory in the Pople–Santry[14] approximation to calculate ^{13}C–^{31}P couplings in CH_3PH_2, CF_3PH_2, $CH_3PH_3^+$ (predicted couplings: −20.87, +42.37, and +7.47, respectively). The change in proceeding to the phosphonium salt reproduces the general trend in phosphine–phosphonium salt pairs.[5] A model based on contact interaction and core polarization contributions to directly bonded nuclei has been investigated by Jameson and Gutowsky[15] to account for trends in signs and magnitudes of nuclear spin coupling constants. The theory has been applied to ^{13}C–^{31}P couplings[16] for P(III), P(IV), and P(V). Qualitative reasoning concerning localized bond descriptions and the relationship between electronegative substituents and s character of orbitals allowed general predictions of couplings which reproduced the gross features of the experimental data.[17]

These investigations represent the available published work on ^{13}C–^{31}P couplings. Systematic inquiry into the nature of the bonding in these compounds, as reflected by their nmr parameters, has been sparse and hampered by the multivalent nature of phosphorus. However, this very aspect may in the long run contribute more to an understanding of the bonding and the nature of spin coupling than more familiar bonding systems. With this view in mind we have made the initial phase toward this goal a systematic investigation of one class of compounds, organophosphonates. Furthermore, the site of variable substitution in these organophosphorus compounds was made one bond removed from the phosphorus atom, on a carbon atom, a factor which hopefully will provide a transition between the progressing knowledge we have of coupling involving only first-row elements and the coupling involving only second-row elements, of which we know very little. The recent studies of Maciel, *et al.*,[18] on ^{13}C–^{13}C, ^{13}C–^{15}N, and ^{13}C–^{19}F nuclear spin couplings point out the increasing difficulty of theoretical methods, in this case the SCF finite-perturbation technique, in dealing with couplings involving group V elements. Much more systematic data are necessary to test new methods of spin coupling theory, d-orbital contributions, and indeed the molecular wave functions themselves.

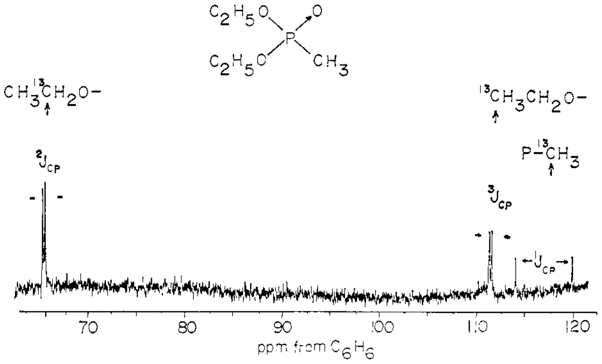

Figure 1. ^{13}C noise-decoupled time-averaged spectrum of $(C_2H_5O)_2P(O)CH_3$. Four scans were accumulated at 2.5 Hz/sec. The spectrometer was locked on the ^{13}C resonance of 60% enriched $^{13}CH_3I$ in a 2-mm capillary tube at 25,144,051.0–6660.0 Hz (lower side band) while the analytical frequency was varied over a range of 1275 Hz. The center of the noise-modulated proton-irradiating field was 99,972,075 Hz, the resonance frequency for the protons in $^{13}CH_3I$. The enhanced signal of the ethoxymethylene carbons results from more nearly resonant proton decoupling. The above spectrum is inverted from the actual output of the spectrometer.

Experimental Section

Instrumentation. ^{13}C spectra were obtained on a Varian HA-100 spectrometer operating at 25.14 MHz in a field/frequency locked mode. The instrument was controlled by a Varian 620-i 8K computer which also served for time averaging. A Varian V-3512-1 provided a noise-modulated proton-decoupling rf field which eliminated C–H splittings in the ^{13}C spectra. The V-4335-1 probe accomodated spinning 8-mm tubes and was double tuned for 25 and 100 MHz. The field/frequency lock signal was derived from the resonance of 60% enriched $^{13}CH_3I$ contained in a sealed 2-mm o.d. capillary tube suspended from a Teflon chuck which could be inserted in the sample tube. Chemical shifts and coupling constants were taken from computer readouts of from usually 10–20 spectral accumulations for signal enhancement and accurate peak placement. The line positions were determined by direct-frequency counting of peaks in scans usually 25–50 Hz in width and are accurate to ±0.2 Hz. Scanning rates were normally 1 Hz/sec. A sample wide-sweep spectrum is shown in Figure 1.

Some of the data were taken with modifications of the standard Varian equipment. In these situations the ^{13}C center band was derived from a 251-MHz signal generated by a Hewlett-Packard 500-MHz synthesizer. This 251-MHz signal, digitally divided by ten and amplified, replaced the crystal-generated rf frequency in the V-4311 rf unit. The analytical frequency sweep was also replaced by a computer-driven Wavetek voltage-controlled oscillator. Using this option, the Varian 620-i computer generates a digital voltage ramp which, under software control, is keyed to the memory locations. The Wavetek oscillator was stable to ±0.1 Hz over a period of hours.

Materials. Most of the phosphonates were of commercial origin, although several were synthesized for the purpose of this investigation.[19] The latter were $(C_2H_5O)_2P(O)CH_3$, $(C_2H_5O)_2P(O)CH_2CHO$, $(C_2H_5O)_2P(O)CH_2OCH_3$, and $(C_2H_5O)_2P(O)CH_2$-

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(9) V. H. Elser and H. Dreeskamp, *Ber. Bunsenges. Phys. Chem.*, 73, 619 (1969).

(10) F. J. Wiegert and J. D. Roberts, *J. Amer. Chem. Soc.*, 91, 4940 (1969).

(11) R. D. Bertrand, F. Ogilvie, and J.G. Verkade, *Chem. Commun.*, 756 (1969).

(12) R. D. Bertrand, F. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, 92, 1908 (1970).

(13) A. H. Cowley and W. D. White, *ibid.*, 91, 1917 (1969).

(14) J. A. Pople and D. P. Santry, *Mol. Phys.*, 8, 1 (1954).

(15) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 51, 2790 (1969).

(16) C. J. Jameson and H. S. Gutowsky, *J. Amer. Chem. Soc.*, 91, 6232 (1969).

(17) The rationale employed here is that developed by H. A. Bent, *Chem. Rev.*, 61, 275 (1961).

(18) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, 92, 1, 11 (1970).

(19) We are indebted to Michael Pickering of the Oregon Graduate Center for carrying out these syntheses.

Table I. ^{13}C Nmr Parameters for Organophosphonates $(C_2H_5O)_2P(O)CH_2X$[a]

X	$^1J_{CP}$	$^2J_{CP}$	$^3J_{CP}$	$\delta_{^{13}CH_2X}$	$\delta_{^{13}CH_2O}$	$\delta_{^{13}CH_3}$
OCH_3[b]	+163.9	−6.4	+5.5	60.99	65.96	111.48
I	+152.7	−6.2	+5.7	139.97	64.13	110.45
H	+143.2	−5.9	+5.9	116.91	66.87	111.53
CN	+141.0	−6.2	+5.7	111.97	64.10	111.67
$CH(OC_2H_5)_2$[c]	+139.0	−6.0	+6.0	95.66	66.39	111.56
$C_6H_4NH_2$[d]	+138.9	−6.6	+6.0	95.68	65.56	111.85
$CH{=}CH_2$	+138.7	−6.7	+5.3	96.05	66.42	111.47
C_6H_5	+137.0	−6.3	+6.0	94.17	66.24	111.52
CH_2Br[e]	+133.9	−6.2	+5.3	96.68	65.90	111.11
$CONH_2$	+132.9	−6.5	+6.0	93.11	65.00	111.88
CH_3[f]	+131.7	−6.0	+5.5	108.75	66.68	111.70
$CO_2C_2H_5$[g]	+131.3	−6.0	+6.1	94.20	66.19	111.90
$COCH_3$[h]	+127			85.5		
CHO	+126.5	−7.3	+5.9	85.14	65.52	111.76
$(CH_3O)_2P(O)CH_3$[i]	+141.8	−6.2		119.04	(76.08)	
$(CH_3CH_2CH_2O)_2P(O)CH_2Cl$[j]	+156.9	−6.6	+6.0	94.70	(59.69)	

[a] $^1J_{CP}$ accurate to ±0.2 Hz, $^2J_{CP}$ and $^3J_{CP}$ accurate to ± 0.1 Hz. Chemical shifts are in parts per million with respect to benzene. A positive shift indicates greater shielding. The experimental shifts are uncorrected for bulk susceptibility differences and are accurate to ±0.02 ppm. The shifts have been placed on the benzene scale by use of the −148.77 ppm shift of benzene from $^{13}CH_3I$ in the same capillary. For convenience of comparison the following shifts (corrected for bulk susceptibility differences) have been determined in this laboratory: dioxane, -88.53; benzene, −149.40, acetic acid (carbonyl carbon), −198.51; and carbon disulfide, −213.83 ppm, all with respect to $^{13}CH_3I$. Signs of couplings based on those found by McFarlane[5] for $(CH_3O)_2P(O)CH_3$. [b] Shift of OCH_3 carbon 67.31 ppm, $^3J_{CP}$ = (+)10.8 Hz. [c] Shifts of substituent ethoxy carbons 66.75 and 112.80 ppm. No observable coupling to phosphorus. [d] Shift of added CH_3OH 78.64 ppm. Amino group para. [e] Shift of CH_2Br 102.65 ppm, $^2J_{CP}$ = (±)1.0 Hz [f] Shift of substituent CH_3 121.17, $^3J_{CP}$ = (−)6.9 Hz. [g] Shifts of substituent ethoxy carbons 67.40 and 113.92 ppm. No observable coupling to phosphorus. [h] Data from ref 8. Shift reported as +85.5 ± 0.5 ppm from benzene. Coupling accurate to ±2 Hz. [i] McFarlane[5] reports $^1J_{CP}$ = +142.2 ± 0.2 Hz, $^2J_{CP}$ = −6.0 ± 0.2 Hz, $\delta_{^{13}CH_3-P}$ +164.2, $\delta_{^{13}CH_3O}$ +121.3 (ppm with respect to external $CH_3{}^{13}COOH$). [j] Shift of CH_3 carbon 118.24 ppm, $-CH_2-$ carbon 104.09 ppm, $^4J_{CP}$ = 0.0 Hz.

$CHCH_2$. All were used as neat liquids except $(C_2H_5O)_2P(O)CH_2C_6H_4NH_2$ and $(C_2H_5O)_2P(O)CH_2CONH_2$, which dissolved with the addition of a few drops of methanol. *p*-Toluidine (practical grade) and acetamide (reagent grade) were examined in dioxane, while ethyl acetate (reagent grade) was used neat. Acetal was purified by distillation.

Computation. Calculations were done on a CDC 3400 computer and required approximately 40 min per molecule.

Results and Discussion

Chemical Shifts. Table I lists the ^{13}C shifts of the relevant carbons encountered in the phosphonates studied. The ethoxy carbon atoms shift very slightly with substituent, while the carbon bonded to the phosphorus exhibits a large chemical shift range of 79 ppm, reflecting the direct electronic effect of the substituent. That this range is not a consequence of a specific substituent interaction with the $(C_2H_5O)_2P(O)$ group is readily apparent when the ^{13}C chemical shifts of the related $^{13}CH_3X$ series are considered. This is shown in Figure 2. The linearity shows that the substituent effects on the phosphonate carbon and that of $^{13}CH_3X$ are proportional and, in fact, equal, as illustrated by the close agreement of any best fit of the points with the unit slope line shown. There appears to be a constant, additive effect of −13.2 ppm on replacing a proton in $^{13}CH_3X$ with the $(C_2H_5O)_2P(O)$ group. This is reasonable in light of the normal deshielding observed in ^{13}C spectra when a more electronegative element is bonded to the ^{13}C being observed (*cf.* $^{13}CH_4 \rightarrow {}^{13}CH_3OH$, −49 ppm and $^{13}CH_4 \rightarrow (^{13}CH_3)_4P^+$, −18 ppm).

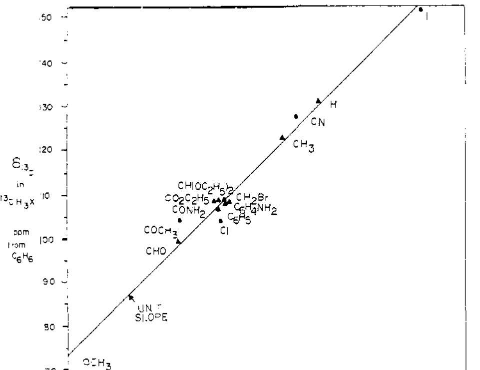

Figure 2. Correlation of the phosphonate carbon chemical shift in $(C_2H_5O)_2P(O)CH_2X$ with the methyl carbon chemical shift in CH_3X.

There is very active research progressing in the theory of ^{13}C chemical shifts.[20–25] This feature assumes relevance when the importance of d-orbital interaction is considered. pπ–dπ back-bonding has been assumed to have much greater importance for second-row than first-row elements.[26,27] Admittedly, most of the pπ–dπ bonding in the phosphonates occurs with the phosphoryl oxygen and to a lesser degree with the ester oxygens. Since the phosphonate back-bone is constant throughout the series, and since the ethoxy carbon chemical shifts are so insensitive to the substituents, the electronic environment around the carbon bonded to the $(C_2H_5O)_2P(O)$ group should be, to a first approximation, constant

(20) J. E. Bloor and D. L. Breen, *J. Amer. Chem. Soc.*, **89**, 6835 (1967).
(21) W. Adam, A. Grimison, and G. Rodriguez, *J. Chem. Phys.*, **50**, 645 (1969).
(22) R. Pugmire, D. M. Grant, M. J. Robins, and R. K. Robins, *J. Amer. Chem. Soc.*, **91**, 6381 (1969).
(23) T. Tokuhiro, N. K. Wilson, and G. Fraenkel, *ibid.*, **90**, 3622 (1968).
(24) T. Tokuhiro and G. Fraenkel, *ibid.*, **91**, 5005 (1969).
(25) A. Jones, D. M. Grant, J. G. Russell, and G. Fraenkel, *J. Phys. Chem.*, **73**, 1624 (1969).
(26) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965, p 83.
(27) R. Hoffman, D. B. Boyd, and S. Z. Goldberg, *J. Amer. Chem. Soc.*, **92**, 3929 (1970).

(neglecting changes in bond angles, etc.). The back-bonding could assume greater importance, however, in cases where electropositive elements are bound to the phosphorus, such as in $[(CH_3)_3P—CH_2X]^+Br^-$ or $(CH_3)_3P{=}CHX$. In cases where X might vary as widely as in the phosphonate series the comparison with the carbon shielding in CH_3X might have significantly poorer agreement.

^{31}P chemical shifts have been previously accumulated for the phosphonates and are listed in Table II. ^{31}P shifts are thought[28] to arise from contributions involving occupation of the dπ orbitals on the phosphorus, imbalance in the σ bonds, and π-bond feedback. For these compounds only the imbalance and ionic character of the σ bonds should be important in accounting for trends within the series. There appears to be a trend toward lower shielding as the electronegativity by X increases. If charge withdrawal from the CH_2 induces charge polarization

$$\overset{\delta-}{P}—\overset{\delta+}{CH_2}—\overset{\delta-}{X}$$

then this would correspond to the expected deshielding of an atom having substituents of greater electronegativity. The limited range of shifts (18 ppm) and the many reversals in expected order make approaches based on a single mechanism such as this highly subject to error and encourage analysis at a later time following more detailed and powerful theoretical models.

Table II. Relevant Chemical Shifts and Coupling Constants

X	$\delta_{^{31}P}$ in $(C_2H_5O)_2$-$P(O)CH_2X^a$	$\delta_{^{13}C}$ in CH_3X^b	$^1J_{CH}$ in CH_3X^c
OCH_3	−22	69.3[d]	140.0[j]
I	−19.8	151.0[d]	151.0[k]
Cl	−18	103.8[d]	148.6[l]
H	−29.4	130.8[d]	125.0[m]
CN		127.5[e]	136.1[e]
$CH(OC_2H_5)_2$		108.6[f]	
$C_6H_4NH_2$		107.7[f]	
$CH{=}CH_2$	−36		
C_6H_5		106.5[g]	136.2[g]
CH_2Br	−28.5	108.1[h]	128[n]
$CONH_2$		106.1[f]	
CH_3	−32.6	122.8[i]	124.9[o]
$CO_2C_2H_5$	−19.0	108.3[f]	130.3[p]
$COCH_3$	−23	104[d]	126.7[p]
CHO		99.1[d]	126.9[p]

[a] In parts per million from 85% phosphoric acid; ref 28. [b] In parts per million with respect to benzene. [c] In hertz. [d] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35,** 722 (1961). [e] G. A. Gray, G. E. Maciel, and P. D. Ellis, *J. Magn. Resonance*, **1,** 407 (1969). [f] This work. CH_3CONH_2 and $CH_3C_6H_4NH_2$ were measured in saturated dioxane solution and corrected to the benzene scale using a shift of 61.39 ppm between benzene and dioxane determined from a 20% solution of benzene in dioxane. $CH_3CH(OC_2H_5)_2$ and $CH_3CO_2C_2H_5$ were used neat, measured with respect to the $^{13}CH_3I$ capillary, and corrected to the benzene scale. No correction was made for bulk susceptibility differences. [g] K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38,** 1216 (1963). [h] P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70,** 841 (1958). [i] E G. Paul and D. M. Grant, *J. Amer. Chem. Soc.*, **85,** 1701 (1963). [j] N. Muller and P. I. Rose, *ibid.*, **84.** 3973 (1962). [k] A. W. Douglas, *J. Chem. Phys.*, **45,** 3465 (1966). [l] A. W. Douglas and D. Dietz, *ibid.*, **46,** 1214 (1967). [m] N. Muller and D. E. Pritchard, *ibid.*, **31,** 768, 1471 (1959). [n] E. R. Malinowski, *J. Amer. Chem. Soc.*, **83,** 4479 (1961). [o] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269,** 385 (1962). [p] G. A. Gray, P. D. Ellis, D. D. Traficante, and G. E. Maciel. *J. Magn. Resonance*, **1,** 41 (1969).

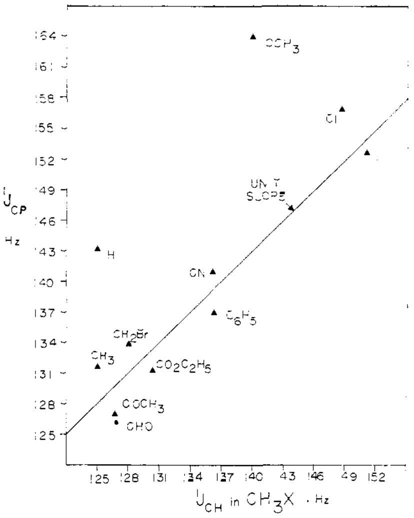

Figure 3. Comparison of the directly bonded ^{13}C–^{31}P coupling constant in $(C_2H_5O)_2P(O)CH_2X$ and the directly bonded ^{13}C–^1H coupling constant in CH_3X.

Coupling Constants. The directly bonded ^{13}C–^{31}P coupling constants vary over a range of greater than 37 Hz or almost 30%. In contrast, the two- and three-bond ^{13}C–^{31}P couplings are essentially insensitive to substitution on the phosphonate carbon. There appears to be a loose relationship between $^1J_{CP}$ and the carbon chemical shift of the substituent carbon atom. The chloro and methoxy compounds deviate considerably, however.

As in the case of the chemical shifts, the series CH_3X can serve as a model system and may, in part, reflect any new effects in a second-row element coupling to carbon. Again, the same general behavior (Figure 3) is noted for the ^{13}C–^{31}P coupling in the phosphonates and the ^{13}C–^1H coupling in CH_3X. The methoxy coupling point is more closely correlated than in the chemical shift correlation but still reflects an apparently high ^{13}C–^{31}P coupling. These overall patterns indicate that phosphorus–carbon couplings exhibit some regular behavior and that trends in these couplings should be amenable to theoretical examination.

Effective Nuclear Charge Variation. The rough correlation of $^1J_{CP}$ with the phosphonate carbon chemical shift, coupled with the above-mentioned relationship between the ^{13}C shift and charge density, forces consideration of charge density variation as instrumental in changes in coupling. Charge density variations have been proposed as having a direct effect on spin coupling constants through variations in the effective nuclear charges of coupled atoms.[29,30] This is felt to have a greater effect on couplings involving protons and less for multielectron atoms. This interpretation has been widely quoted and used to explain variations in nuclear spin couplings. However, detailed calculations using the SCF–finite-perturbation approach[18] caution that although increased nuclear-charge-induced variations of the amplitude of the s orbitals involved in

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(28) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5,** 169 (1967).

(29) D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, **87,** 3994 (1965).

(30) W. M. Litchman and D. M. Grant, *ibid.*, **89,** 6775 (1967).

the coupling may help correct certain theoretically predicted couplings to values more in line with experiment, by no means is this true in general. In regard to the phosphonates, a model comparison can be of aid in determining the nature of the $^{13}C-^{31}P$ bond and the predicted $^{13}C-^{31}P$ coupling on the basis of the above arguments. The transition from $(CH_3)_3P-H^+$ to $(CH_3O)_2P(O)H$ should give a crude estimation of the contribution of a variation of effective nuclear charge to the P–H coupling for the indicated substituent variation within an isolated-bond model. The P–H coupling increases from +505 Hz[31] in the former to +695 Hz[3] in the latter, an increase of 37.6%. Certainly no multiple bonding to the hydrogen occurs and, although it can be conjectured that the bonding to the oxygen involves more p character than that normally used in the sp^3 hybrid orbital, this implies an even higher P–H coupling due to the enriched s character in the phosphorus hybrid orbital participating in the P–H bond. This same phosphorus hybrid orbital in $(CH_3)_3P-H^+$ is definitely closer to pure sp^3 since the electronegativities of carbon and hydrogen are much more nearly equal. Thus, within the hypothesis of s-orbital distribution within hybrid orbitals to substituents of differing electronegativity and the framework of effective nuclear charge arguments, the percentage increase noted above should be representative for the indicated substituent variation. This is not the case, however, as the very closely related situation involving a $^{13}C-^{31}P$ coupling, $(CH_3)_3P-CH_3^+$ (+56.5 Hz)[9] to $(CH_3O)_2P(O)CH_3$ (+142.2 Hz),[5] exhibits an increase of 152%, over four times the supposed increase. This drastic difference in percentage increase suggests that either the above factors are not controlling the changes in couplings, or that additional contributions may be important.

s-Character Concept. The other main parameter which has been used to correlate spin–spin coupling data is the "s character" of the hybrid orbitals participating in the bonding between the coupled nuclei. This received its first application in regard to $^{13}C-^{1}H$ coupling constants[32,33] and has been used to varying degrees since then.[34–45] There have been several alternate interpretations on the basis of the importance of changes in effective nuclear charge,[29,30,46,47] ionic character,[48] and "average triplet excitation energy, ΔE."[49,50] The theoretical basis for the correlation of s character and the $^{13}C-^{1}H$ coupling constant rests on developments of Ramsey's[51] second-order perturbation treatment of the Fermi contact term within the average sum over states, or ΔE approximation. Using valence-bond[52,53] or LCAO-MO[33,54] approaches, the simple expression

$$J_{CH} = \frac{16h\beta^2\gamma_C\gamma_H}{9\Delta E} S_C^2(0)S_H^2(0)P^2{}_{s_Cs_H}$$

was developed. The $S_C^2(0)$ and $S_H^2(0)$ are the carbon 2s orbital and hydrogen 1s orbital densities at their respective nuclei, γ is the magnetogyric ratio, β is the Bohr magneton, h is Planck's constant, and $P^2{}_{s_Cs_H}$ is the carbon 2s–hydrogen 1s bond order.

The most crippling aspect of this theory is its inability to predict negative reduced coupling constants. Negative values for reduced $^{13}C-^{31}P$ couplings are common[2,5] for both directly bonded and long-range situations. The $^2J_{CP}$'s in the phosphonates are negative (based on McFarlane's[5] work on $(CH_3O)_2P(O)CH_3$). This approach has also run into difficulty in rationalizing the very large $^{13}C-^{1}H$ couplings in substituted methanes.

Approximate Theoretical Methods for Nuclear Spin Coupling. Since the early MO and VB treatments more sophisticated attempts have been made to explore the relationship between spin coupling, s character, and bond orders.[13–15,55–75]

Many of these treatments rely on the Pople–Santry[14] method of summing over a truncated set of excited states. This method was able to predict changes in sign of J as the above expression cannot, but has not been particularly successful in predicting trends or magnitudes. A much more promising technique is the approximate SCF–finite-perturbation technique of Pople.[18,76–79]

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(31) H. Dreeskamp, H. Elser, and C. Schumann, *Ber. Bunsenges. Phys. Chem.*, **70**, 751 (1966).

(32) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959).

(33) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959).

(34) E. R. Malinowski, *J. Amer. Chem. Soc.*, **83**, 4479 (1961).

(35) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

(36) N. Muller and P. I. Rose, *J. Amer. Chem. Soc.*, **84**, 3973 (1962).

(37) A. W. Douglas, *J. Chem. Phys.*, 40, 2413 (1964).

(38) H. Dreeskamp and E. Sackmann, *Z. Phys. Chem. (Frankfurt am Main)*, **34**, 273 (1962).

(39) N. Muller, *J. Chem. Phys.*, **42**, 4309 (1965).

(40) G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 1818 (1966).

(41) G. J. Karabatsos, *ibid.*, **83**, 1230 (1961).

(42) D. F. R. Gilson, *J. Chem. Phys.*, **44**, 4036 (1966).

(43) A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *J. Amer. Chem. Soc.*, **91**, 527 (1969).

(44) C. H. Yoder, K. H. Tuck, and R. E. Hess, *ibid.*, **91**, 539 (1969).

(45) C. D. Cook and K. Y. Wan, *ibid.*, **92**, 2595 (1970).

(46) J. I. Musher, *Proc. Colloq. AMPERE (Nucl. Magn. Resonance Relaxation Solids)*, 13, 360 (1965).

(47) J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965).

(48) T. L. Brown and J. C. Puckett, *J. Chem. Phys.*, **44**, 2238 (1966).

(49) A. Saika, *ibid.*, **45**, 2715 (1966).

(50) Y. Kato and A. Saika, *ibid.*, **46**, 1975 (1967).

(51) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

(52) M. Karplus and D. M. Grant, *Proc. Nat. Acad. Sci. U. S.*, **45**, 1269 (1959).

(53) H. S. Gutowsky and C. Juan, *J. Chem. Phys.*, **37**, 2198 (1962).

(54) H. M. McConnell, *ibid.*, **24**, 460 (1956).

(55) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962).

(56) D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963).

(57) K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963).

(58) D. S. Bartow and J. W. Richardson, *ibid.*, **42**, 4018 (1965).

(59) T. Yonezawa, I. Morishina, and M. Fujii, *Bull. Chem. Soc. Jap.*, **38**, 1224 (1965); **39**, 2110 (1966).

(60) J. A. Pople and D. P. Santry, *Mol. Phys.*, **9**, 311 (1965).

(61) R. C. Fahey, C. G. Graham, and R. L. Piccioni, *J. Amer. Chem. Soc.*, **88**, 193 (1966).

(62) F. B. Van Duijneveldt, V. M. S. Gil, and J. N. Murrell, *Theor. Chim. Acta*, **4**, 85 (1966).

(63) J. N. Murrell and V. M. S. Gill, *ibid.*, 4, 114 (1966).

(64) J. N. Murrell, P. E. Stevenson, and G. T. Jones, *Mol. Phys.*, **12**, 2656 (1967).

(65) R. Ditchfield, M. A. Jensen, and J. N. Murrell, *J. Chem. Soc. A*, 1674 (1967).

(66) A. H. Cowley, W. D. White, and S. L. Manatt, *J. Amer. Chem. Soc.*, **89**, 6433 (1967).

(67) N. Cyr and T. J. R. Cyr, *J. Chem. Phys.*, 47, 3082 (1967).

(68) C. Barbier and G. Berthier, *Theor. Chim. Acta*, **9**, 92 (1967).

(69) C. Barbier and G. Berthier, *Int. J. Quantum Chem.*, 1, 657 (1967).

(70) R. Ditchfield and J. N. Murrell, *Mol. Phys.*, **14**, 481 (1968).

(71) A. H. Cowley and W. D. White, *J. Amer. Chem. Soc.*, **91**, 1913 (1969).

(72) G. A. Gray, P. D. Ellis, D. D. Traficante, and G. E. Maciel, *J. Magn. Resonance*, 1, 41 (1969).

(73) G. A. Gray, G. E. Maciel, and P. D. Ellis, *ibid.*, 1, 407 (1969).

(74) M. Barfield, *J. Chem. Phys.*, **48**, 4458, 4463 (1968).

(75) A. C. Blizzard and D. P. Santry, *Chem. Commun.*, 87 (1970).

(76) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 47, 2026 (1967).

(77) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *Chem. Phys. Lett.*, 1, 456 (1967).

(78) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960, 2965 (1968).

(79) N. S. Ostlund, M. D. Newton, J. W. McIver, Jr., and J. A. Pople, *J. Magn. Res.*, 1, 185 (1969).

Table III. SCF–Finite-Perturbation Calculations for $(CH_3O)_2P(O)CH_2X$

	X: OCH$_3$	Cl	H	CN	CH$_3$	CHO
			C–P			
$^1J_{CP}$	182.31	167.91	146.25	133.76	154.69	134.10
$\Delta ^1J_{CP}$[a]	+18.4	+11.0	+3.0	−7.2	+23.0	+7.6
$^1J_{CP}$(corr)[b]	188.21	163.71	137.09	127.15	146.40	124.56
$\Delta ^1J_{CP}$(corr)	+19.3	+6.8	−6.1	−13.8	+14.7	−1.9
$P^2{}_{S_CS_P}$	0.07680	0.07394	0.07148	0.06598	0.06895	0.06749
			C–H			
$^1J_{CH}$	116.46	114.97	112.91	123.57	109.45	99.05
$^1J_{CH}$(corr)	115.89	113.21	131.77	125.50	140.55	121.42
$^2P_{S_CS_H}$	0.2354	0.2346	0.2317	0.2226	0.2222	0.2216
			Charge Densities (X = ABC)			
Q(P)	3.622	3.609	3.600	3.583	3.603	3.595
Q(C)	3.985	4.078	4.198	4.156	4.169	4.226
Q(O)	6.653	6.656	6.663	6.652	6.664	6.659
Q(–O–)	6.423	6.426	6.428	6.424	6.429	6.427
$Q(CH_3)$	3.810	3.810	3.809	3.810	3.810	3.810
$Q(H_2)$	1.011	0.989	0.972	0.958	0.984	0.946
Q(A)	6.239	7.053	0.962	3.887	3.919	3.699
Q(B)	3.751			5.192	1.014	1.024
Q(C)	1.035					6.283
			Other Couplings			
$^1J_{CC}$				95.26	36.25	36.27
$P^2{}_{S_CS_C}$				0.1103	0.0568	0.0782
$^2J_{CH}$					6.46	14.22
$^2J_{CC}$	−6.72					
$^2J_{CN}$				8.70		

[a] Calculated value for $^1J_{CP}$ in $(CH_3O)_2P(O)CH_2X$ minus experimental value for $^1J_{CP}$ in $(C_2H_5O)_2P(O)CH_2X$ ($(C_3H_7O)_2P(O)CH_2Cl$ for X = Cl). [b] Corrected for variations in effective nuclear charge (see text).

In this technique the coupling constant is computed by computing the INDO (intermediate neglect of differential overlap) molecular orbital wave function[76] in the presence of a contact perturbation in a self-consistent fashion.[77,78]

$$h_B = (8\pi/3)\beta\mu_B S_B{}^2(0)$$

The reduced coupling constant $K_{AB} = (2\pi J_{AB}/\hbar\gamma_A\gamma_B)$ is then expressed as

$$K_{AB} = (8\pi/3)\beta^2 S_A{}^2(0)S_B{}^2(0)\left(\frac{\delta}{\delta h_B}\rho_{S_AS_A}(h_B)\right)_{h_B=0}$$

$\rho_{S_AS_A}$ is the diagonal spin density matrix element for the valence s orbital of atom A. Maciel, *et al.*,[18] employed this method in the consideration of directly bonded ^{13}C–^1H, ^{13}C–^{13}C, ^{13}C–^{15}N, and ^{13}C–^{19}F couplings. Good agreement between calculated and experimental ^{13}C–^1H coupling was reached for hydrocarbons and substituted hydrocarbons of type $-I^+$, but rather poorer agreement for substituents of type $-I^-$. The ^{13}C–^{13}C couplings again exhibited an overall trend of $^1J_{CC}$ with $P^2{}_{S_AS_B}$. Within hybridization types, however, much more scatter was evident, with some reversals. The computed $^1J_{CC}$ was much more reliable in comparison with experiment especially in the progression sp^3–sp^3, sp^3–sp^2, sp^3–sp. No simple relationship was found between $^1J_{CN}$ and $P^2{}_{S_CS_N}$, casting doubt on the validity of relating ^{13}C–^{15}N coupling constants to carbon and nitrogen s characters. Poor comparisons of experimental and theoretically predicted ^{13}C–^{19}F coupling were achieved, leading to suspicion of significant contribution from spin dipolar and/or orbital coupling mechanisms or inaccuracy in the INDO wave functions. The former may be more probable, as pointed out in calculations of ^{19}F–^{19}F couplings in fluoroethanes by Blizzard and Santry.[75] Their calculations show that the orbital contribution to the ^{19}F–^{19}F coupling completely overshadows the contact contribution and that no scaling of the $S_F{}^2(0)$ proved to be necessary to bring reasonable agreement between theory and experiment.

In view of the success achieved in predicting spin coupling constants using the INDO–finite-perturbation scheme, a set of model calculations was attempted on the phosphonates. In order to conserve computing time the calculations were for the series

$$(CH_3O)_2\text{–}P(O)\text{–}CH_2\text{–}X$$

Standard geometries[18] were used for bonds involving all atoms but phosphorus. A phosphoryl P–O distance of 1.47 Å and ester P–O distance of 1.54 Å were used with tetrahedral angles about the phosphorus. The P–C distance was selected as 1.81 Å. Figure 4 illustrates the geometry used for the $(CH_3O)_2P(O)$–CH_2 group. Of course, the spin couplings observed in experiment are those for the time-averaged rotamers. The calculation refers to only one conformer, but the

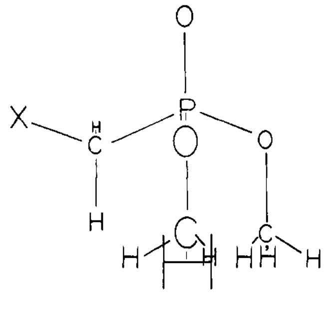

Figure 4. Geometry of the $(C_2H_5O)_2P(O)CH_2$ group used in the SCF–finite-perturbation calculations.

Table IV. Comparison with Related CH_3X and CH_3CH_2X Systems

	X: OCH_3	Cl	H	CN	CH_3	CHO
			SCF–Finite-Perturbation Values			
${}^1J_{CP}{}^{P-CH_2X}$	182.31	167.91	146.25	133.76	154.69	134.10
${}^1J_{CH}{}^{P-CH_2X}$	116.46	114.97	112.91	123.57	109.45	99.05
${}^1J_{CH}{}^{CH_3X}$ [a]	135.5		122.9	122.5	122.1	121.4
${}^1J_{CC}{}^{CH_3CH_2X}$ [a]	49.6[b]		41.5	40.7	42.1	
${}^1J_{CC}{}^{CH_3X}$ [a]				76.7	41.5	64.0
$(S_P{}^2(0)/S_C{}^2(0))(\gamma_P/\gamma_C)({}^1J_{CC}{}^{CH_3CH_2X})$	162.3		135.8	133.2	137.8	
$(S_P{}^2(0)/S_C{}^2(0))(\gamma_P/\gamma_C)({}^1J_{CC}{}^{CH_3X})$				251.0	135.8	205.5
$P^2{}_{s_Cs_H}{}^{P-CH_2X}$	0.2354	0.2346	0.2317	0.2226	0.2222	0.2216
$P^2{}_{s_Cs_H}{}^{CH_3X}$ [a]	0.2615		0.2485	0.2385	0.2411	0.2392
$P^2{}_{s_Cs_C}{}^{CH_3CH_2X}$ [a]	0.06718		0.06200	0.05881	0.06017	
			Experimental Values			
${}^1J_{CP}$	163.9	156.9	143.2	141.0	131.7	126.5
${}^1J_{CH}{}^{CH_3X}$ [c]	140.0	148.6	125.0	136.1	124.9	126.9
${}^1J_{CC}{}^{CH_3CH_2X}$	(37.7)[d]		34.6[e]	33.0[f]		
${}^1J_{CC}{}^{CH_3X}$				56.5[f]	34.6[e]	39.4[g]

[a] Reference 18. [b] Value for X = OH used from ref 18. [c] See Table II. [d] F. J. Weigert, Thesis, California Institute of Technology, 1968, p 110. [e] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962). [f] Reference 73. [g] Reference 72.

trends within the series hopefully should be reproduced. Rotamer preference should occur to a high degree only when intramolecular hydrogen bonding is important. This is possible with a number of the phosphonates. The substitution of methoxy for ethoxy should also have a small but constant effect. Experimentally, $(CH_3O)_2P(O)CH_3$ has a ${}^{13}C-{}^{31}P$ coupling of +141.8 Hz as compared to +143.2 Hz in $(C_2H_5O)_2P(O)CH_3$. The value used for $S_P{}^2(0)$ was 5.6251.[80] The CNDO approximation was used for the second-row elements. No d orbitals were used in construction of the wave functions. The results are given in Tables III and IV. The perturbation was placed on the phosphonate carbon since more observable one-bond couplings were available this way. The effect of placing the perturbation on a second-row element is untested, and for the purposes of calculations of coupling involving a second-row element it was decided that placing the perturbation on the carbon atom generated fewer uncertainties in interpretation.

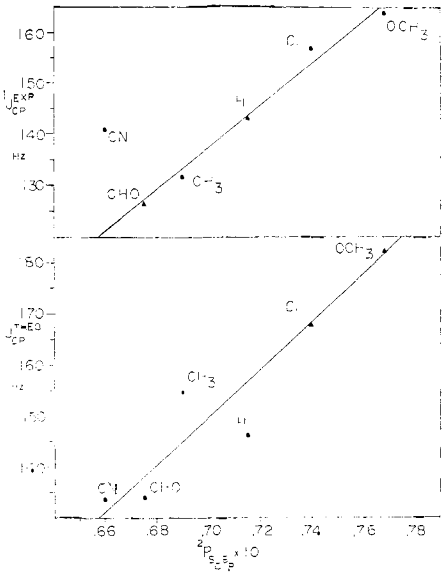

Figure 5. Correlation of the experimental and theoretically calculated directly bonded ${}^{13}C-{}^{31}P$ coupling constants with $P^2{}_{s_Cs_P}$.

The predicted ${}^{13}C-{}^{31}P$ one-bond couplings agree quite favorably with the experimental results in terms of magnitude and range of values. The range of experimental values is 39.4 Hz, while that of the calculated couplings is 48.5 Hz, only a 5% greater range than that given by experiment. The order is essentially the same as the experimental order except for the methyl substituent. The absolute agreement is excellent for X = H, CN, and CHO, only +2, −5, and +6% error, respectively. The calculations for the OCH_3 and Cl cases are +11 and +7% in error, while the methyl value is most in error at +17%. These errors compare favorably with those for the calculated[18] ${}^1J_{CC}$ for ${}^{13}CH_3{}^{13}CH_2X$ given in Table IV. Evidently, replacement of a methyl group by the $(CH_3O)_2P(O)$ group does not affect the sensitivity of the coupling mechanism to substituent effects, as shown by the good correlation of theoretical and experimental ${}^1J_{CP}$ couplings in $(C_2H_5O)_2P(O)CH_2X$ with the respective ${}^1J_{CC}$ in CH_3CH_2X (corrected for the greater $S_P{}^2(0)$ and magnetogyric ratio). Table III shows a general trend of $P^2{}_{s_Cs_P}$ with ${}^1J_{CP}$ (experimental) or ${}^1J_{CP}$ (theoretical). Figure 5 shows the close correlation of the experimental ${}^1J_{CP}$ for the phosphonates with the calculated $P^2{}_{s_Cs_P}$ for the model compounds. Only the cyano compounds deviates. Both correlations in Figure 5 exhibit approximately the same sensitivity or slope. The range of $P^2{}_{s_Cs_P}$ is only 16% compared with the 30% experimental and 36% theoretical ranges. This is in contrast to the case for ${}^{13}C-{}^{13}C$ coupling where both ${}^1J_{CC}$ (theoretical) and $P^2{}_{s_Cs_C}$ varied approximately with the same sensitivity, but much less than the experimental ${}^1J_{CC}$.[18]

The calculated charge densities allow an assessment of the effect of variations in effective nuclear charge. Table III contains couplings which have been "corrected" for variation of charge density at the nuclei. These resulted from multiplication of the theoretical coupling by the factors $\{(3.25 - 0.35q_C)/3.25\}^3$ for carbon and $\{1.0 - 0.30q_H\}^3$ for hydrogen. No correction was made for phosphorus since the calculated charge densities vary over such a small percentage

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(80) J. R. Morton, J. R. Rowlands, and W. H. Whiffen, *Nat. Phys. Lab. (U. K.), Rept.*, BPR 13 (1962).

range. As in the case of $^{13}C-^{13}C$ coupling,[18] variations in charge density do not help bring the theoretical couplings closer to overall agreement with experiments.

Several other couplings are available for the phosphonate carbon. Again, replacing a proton in CH_3X by the $(CH_3O)_2P(O)$ group does not seem to affect drastically the expected results. For example, in the phosphonate model series there are three cases of theoretically calculated directly bonded $^{13}C-^{13}C$ couplings. A comparison between these theoretical values and analogous $^{13}C-^{13}C$ couplings (theoretical and experimental) in CH_3CN, CH_3CH_3, and CH_3CHO (as shown in Table IV), indicates that, except for the high value of the cyano case, these couplings in the phosphonates parallel those in the above compounds. Note that the theoretical value for the cyano compound is also high in the $^1J_{CC}$ calculation for CH_3CN.[18] A reversal is seen between the calculated $^1J_{CC}$ and $P^2{}_{S_CS_C}$ in $(CH_3O)_2P(O)CH_2CH_3$ and $(CH_3O)_2P(O)CH_2CHO$. Both $^2J_{CH}$ couplings for these compounds are calculated positive here. The analogous couplings in CH_3CH_3 and CH_3CHO are -4.5[55] and $+26.6$ Hz,[81] respectively. The calculated $^2J_{CN}$ in the cyano phosphonate has the same sign but is almost more than three times the magnitude of the analogous[2] J_{CN} in CH_3CN.

The calculated charge densities are consistent with the phosphonate carbon chemical shifts within the above-discussed concept of deshielding by electronegative substituents.[20-25] This relationship is depicted in Figure 6. The slope gives approximately 250 ppm per electronic charge as compared to 160 ppm in aromatic hydrocarbons.[82-84] It is not clear whether it is the limited nature of the data which leads to this high result or that 160 ppm/electron is only valid for aromatic hydrocarbons and heterocyclic aromatics. The CHO point deviates significantly from the correlation. The aldehyde fragment is the only $-I^-$ substituent among the model compounds. As has been noted,[18] $-I^-$ substituents have been difficult to treat using the INDO approximation. Extended explanation of this effect should await calculation of the other rotamers so that a more meaningful charge density may be considered. This might also considerably change the slope of a charge density–chemical shift correlation to that more in line with previous investigations.

The calculated phosphorus charge densities do not correlate at all with the ^{31}P chemical shifts. Table III shows little change in the oxygen charge densities, so that the principal effect on the phosphorus is that of the CH_2X group. The phosphorus charge densities cover a very small range. The main factors responsible for the ^{31}P shift are difficult to identify since, in these cases, no single relationship exists between the phosphorus chemical shift and the calculated parameters. Again rotamer-averaged charge densities could correlate more closely with observed chemical shifts. Attention should also be paid to possible intermolecular association.

Jameson and Gutowsky's[15,16] theory is difficult to apply quantitatively to compounds of small chemical differences, but certainly in a P–CH_2–X bonding situation,

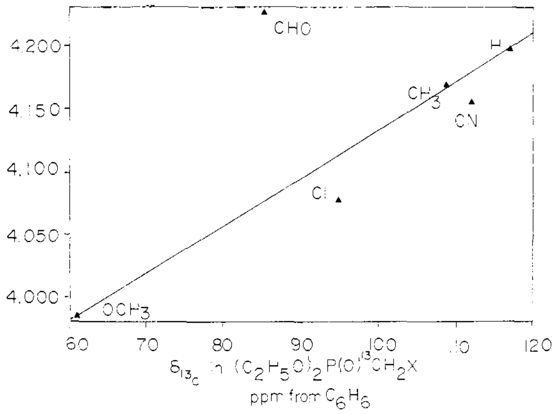

Figure 6. Comparison of experimental phosphonate carbon chemical shift and the calculated phosphonate carbon charge density.

according to their theory, the $^{13}C-^{31}P$ coupling should increase as more p character is used in the carbon orbital involved in bonding to X. This assumes that the loss of s character from this orbital is distributed to the bonding orbitals directed toward the hydrogens and the phosphorus atom. Thus X = H should produce the smallest $^{13}C-^{31}P$ coupling since it possesses the smallest electronegativity of all the substituents examined. However, $(C_2H_5O)_2P(O)CH_2-H$ has one of the higher $^{13}C-^{31}P$ couplings, greater than that of any of the carbon-bonded substituents. The good correlation of $P^2{}_{S_CS_P}$ with $^1J_{CP}$ indicates that the s-character viewpoint may be accommodated but reversals (as in the CH_3, H case here) are expected to occur, as shown[18] in $^{13}C-^{13}C$ couplings. Further SCF–finite-perturbation calculations on P(III) and P(V) systems should shed light on the reliability of the s-character hypothesis for P(IV) compounds and the necessity for involving core polarization in P(III) compounds. The latter should be especially interesting in view of the very recent sign determination for $^1J_{CP}$ in CH_3PCl_2 by Albrand and Gagnaire[85] as negative. Jameson and Gutowsky's theory predicts $^1J_{CP}$ getting more positive as more electronegative groups are substituted on P(III). The opposite is true in going from $(CH_3)_3P$ to CH_3PCl_2.

Conclusion

A systematic investigation of the ^{13}C high-resolution nmr parameters of a closely related series of organophosphorus compounds has been undertaken. The diethyl phosphonates $(C_2H_5O)_2P(O)CH_2X$ were chosen in an effort to minimize direct perturbations of the phosphorus and provide a transition from the expanding knowledge of chemical shifts and spin couplings of first-row elements. The phosphonate carbon shows a large chemical shift range of 79 ppm, while the $^{13}C-^{31}P$ one-bond couplings run from +163.9 to +126.5 Hz. There appears to be no specific interaction of the $(C_2H_5O)_2P(O)$ group with the X substituent since the phosphonate carbon chemical shifts correlate very well with the analogous CH_3X carbon chemical shifts.

Approximate self-consistent-field–LCAO–MO calculations involving the finite perturbation technique are successful in predicting the magnitudes, signs, and relative ordering of the $^{13}C-^{31}P$ one-bond couplings for a

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(81) H. Dreeskamp and E. Sackmann, "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press, New York, N. Y., 1965, p 143.

(82) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).

(83) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, 41, 966 (1963).

(84) P. C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 1838, 1846 (1961).

(85) J. P. Albrand and D. Gagnaire, *Chem. Commun.*, 874 (1970).

related series of phosphonates. The experimental $^1J_{CP}$ correlates linearly with the C–P s-bond order, $P^2_{s_C s_P}$, although the bond orders vary over about half the percentage range that is evidenced by either the experimental or theoretical couplings.

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Infrared Spectra of the Pyrolysis Products of Borane Carbonyl in an Argon Matrix

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Abstract: Infrared spectra of the pyrolysis products of BH_3CO trapped in low-temperature matrices have been obtained. Bands observed at 2808, 1604, and 1125 cm^{-1} cannot be attributed to B_2H_6, BH_3CO, CO, or any known molecule containing boron and oxygen. Based on the ^{10}B isotope shifts and the special conditions required for isolation, these unidentified bands are assigned to the simple borane, BH_3. Under certain pyrolysis conditions bands at 1403, 1378, and 910 cm^{-1} are also observed. The molecule associated with these bands is identified as boroxine ($H_3B_3O_3$) from the observation of dilute-matrix spectra of that compound. Another molecule, $H_2B_2O_3$, may be found in the pyrolysis reaction if traces of O_2 are present in the gas mixture.

Borane has long been postulated as a kinetic intermediate in the reaction of boron hydrides, but it has never been isolated.[1,2] Attempts to isolate BH_3 and identify it by optical spectroscopy have proved to be inconclusive.[3–6] Mass spectrometric techniques for the study of the pyrolytic decomposition of B_2H_6 and BH_3CO only recently have become refined sufficiently for the direct identification of BH_3 in small concentration.[7–12] Of the possible experimental methods for spectroscopic study of BH_3, low-temperature matrix isolation appeared to be the most promising.[13]

Pyrolysis experiments have shown that under certain experimental conditions BH_3 is produced in good yield by the thermal dissociation of BH_3CO. In their studies Mappes and Fehlner[14] have proposed the reaction sequence

$$BH_3CO \longrightarrow BH_3 + CO \qquad (1)$$

$$BH_3 + BH_3 \longrightarrow B_2H_6 \qquad (2)$$

$$BH_3 + \text{wall} \longrightarrow B + {}^3/_2H_2 + \text{wall} \qquad (3)$$

To maximize the BH_3 yield and reduce the extent of reactions 2 and 3, the residence time of BH_3 was reduced as low as 10^{-4} sec and the BH_3CO reactant was diluted with helium and pyrolyzed at high pressures (5 mm) and high flow rates. At 700°K a borane yield of 50% (based on borane carbonyl decomposed) was claimed. In this work we are reporting on the results of experiments in which the fast-flow pyrolysis technique used by Mappes and Fehlner was combined with the matrix-isolation technique in an attempt to obtain the infrared spectrum of BH_3.

Experimental Section

A. Cryostat. A helium dewar with a rotatable tail was used in these experiments The target and external windows were CsI. A third window was available for the observation of the film growth. A target window was placed in the copper block at the tail of the dewar against an indium O-ring made of 0.030 wire and the assembly was jammed tight with a screwcap. A small hole was drilled into the CsI window to its center and an Au–2.1%Co *vs.* Cu thermocouple was imbedded by packing it into the hole with indium wire. Apiezon-L was used to enhance thermal contact. The temperature, measured for the bulk CsI crystal, was monitored during all experiments. The pump-out arm of the dewar tail served as the vacuum jacket for the various pyrolysis sources. All the sources were built of quartz onto a 55/50 female ground joint. The hot zone was 30 cm from the ground joint, the tip of the pyrolysis tube 2 cm from

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(1) R. M. Adams, "Boron Metals—Boron Compounds and Boranes," Wiley-Interscience, New York, N. Y., 1964.

(2) A. E. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(3) J. R. Morrey, A. B. Johnson, Y.-C. Fu, and G. R. Hill, *Advan. Chem. Ser.*, No. 32, 157 (1961).

(4) G. E. Leroi, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1960.

(5) S. H. Bauer, G. Herzberg, and J. W. C. Johns, *J. Mol. Spectrosc.*, 13, 256 (1964).

(6) S. H. Garnett, Ph.D. Thesis, Princeton University, Princeton, N. J., 1968.

(7) A. Baylis, G. A. Pressley, Jr., and F. E. Stafford, *J. Amer. Chem. Soc.*, **88**, 2428 (1966).

(8) J. H. Wilson and H. A. McGee, Jr., *J. Chem. Phys.*, **46**, 1444 (1967).

(9) P. S. Ganguli and H. A. McGee, Jr., *ibid.*, **50**, 4658 (1970).

(10) T. P. Fehlner and G. W. Mappes, *J. Phys. Chem.*, **73**, 873 (1969).

(11) T. P. Fehlner and W. S. Koski, *J. Amer. Chem. Soc.*, **87**, 409 (1965).

(12) O. Herstad, G. A. Pressley, Jr., and F. E. Stafford, *J. Phys. Chem.*, 74, 874 (1970).

(13) The field of matrix isolation was very extensively reviewed recently by T. S. Hermann and S. R. Harvey, *Appl. Spectrosc.*, **23**, 435 (1969).

(14) G. W. Mappes and T. P. Fehlner, *J. Amer. Chem. Soc.*, **92**, 1562 (1970). The authors would like to thank Professor Fehlner for a preprint of this paper.