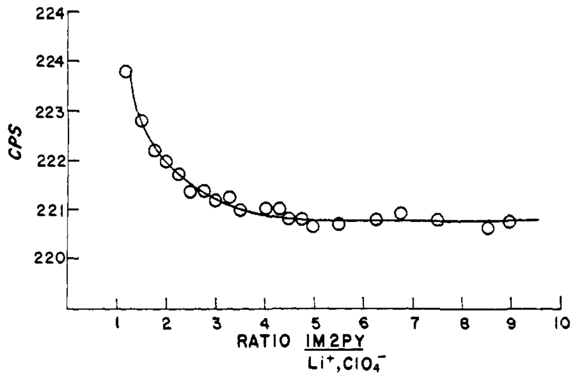

Figure 7. Chemical shift of the dioxane protons *vs.* 1M2PY/$LiClO_4$ mole ratio.

Na^+ ion is solvated by four molecules of tetrahydrofuran.

The resonance of the dioxane protons was also studied as a function of lithium perchlorate concentration. The results are shown in Figure 7. At low ratios of 1M2PY:$LiClO_4$, the dioxane protons undergo an appreciable shift. It is possible, therefore, that at low concentration of 1M2PY dioxane participates in the solvation of the lithium ion. These results also support the hypothesis that the low-energy far-infrared band, which appears at low ratios, is a result of the participation of the dioxane in the solvation of the lithium ion.

Attempts were made to study the solvation of alkali metal ions in 1M2PY by ultraviolet and Raman spectroscopy. The ultraviolet spectrum of 1M2PY is featureless from 380 mμ to the solvent cutoff at 265 mμ. Spectra of solutions of 1.0 *M* lithium perchlorate, 0.6 *M* sodium tetraphenylborate, and 0.8 *M* sodium perchlorate were obtained from 380 to 265 mμ with negative results. The sodium tetraphenylborate solution exhibited absorption due to the anion.

Raman spectra in the 1700–200-cm^{-1} spectral regions were obtained of 1.0 *M* solutions of lithium chloride, lithium bromide, and lithium perchlorate in 1M2PY. Three anions were chosen in order to observe possible anion effects. Lithium perchlorate solution showed a band near 400 cm^{-1}, but this band was not present in the chloride or bromide solutions and was due to the perchlorate anion. No bands which could be attributed to salt–solvent interaction were discovered. The absence of Raman bands seems to indicate that the ion–solvent interaction is largely ionic as postulated by Edgell, *et al.*[2e]

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Dynamic Polarization of Phosphorus-31 Nuclei. Some Effects of Chemical Environment

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Abstract: Quantitative phosphorus nmr enhancements, determined from dynamic nuclear polarization measurements at 74 G, are reported for a variety of phosphorus-containing compounds in solution with the free radical bisdiphenylenephenylallyl. The wide range of observed enhancements, from −650 for $(MeO)_3PO$ to +1610 for PCl_3, indicates that ^{31}P contact relaxation components are particularly responsive to changes in the chemical environment of phosphorus. For substituted phosphates, phosphites, and phosphines, the magnitude of the scalar interaction depends critically on the substituents at P. In order of increasing scalar interaction H < Cl < Br < C_6H_5 < RO. This, coupled with the irregular behavior of thio-substituted compounds, suggests the presence of both direct and indirect coupling mechanisms, the former related to electron–nucleus distance of closest approach, the latter to changes in complexation tendencies.

Previous dynamic nuclear polarization studies of ^{31}P nuclei at both low[2] and high[3] external magnetic fields have shown that the coupling between P nuclei and the electrons of dissolved free radicals is strongly dependent upon the chemical composition of the system. With tri-*t*-butylphenoxyl (TTBP) as the free radical, many systems were unstable and only the sign of the enhancement could be obtained. However, this was sufficient to demonstrate several broad features, the most striking of which was the observation that trivalent phosphorus compounds gave more positive enhancements than their pentavalent counterparts. Recently, we discovered that the free radical bisdiphenylenephenylallyl (BDPA) forms solutions with almost any phosphorus-containing compound which are stable indefinitely; this allowed quantitative measurements to

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[2] J. A. Potenza, P. J. Caplan, and E. H. Poindexter, *J. Chem. Phys.*, **49**, 2461 (1968).

[3] (a) R. A. Dwek and R. E. Richards, *Chem. Commun.*, 581 (1966); (b) P. W. Atkins, R. A. Dwek, J. B. Reid, and R. E. Richards, *Mol. Phys.*, 13, 175 (1967).

be performed. Here, we report the results of such measurements and show that the degree of scalar coupling between radical and solvent follows in a regular way the local stereochemistry of phosphorus.

Theory

For a system of two coupled spins, one from the odd electron of a free radical, the other from solvent magnetic nuclei, the magnitude of the nmr signal enhancement, arising from dynamic polarization, is given by

$$G = \frac{\gamma_e}{\gamma_n} \frac{(r - s + c)}{(2q + r + s + c)} \left(\frac{T_B - T_1}{T_B} \right) S_e(P) \quad (1)$$

The enhancement magnitude G depends on four factors, the first of which is γ_e/γ_n, the ratio of the gyromagnetic ratio of the electron to that of the nucleus. This sets upper and lower limits for the zero-field enhancement since the remaining factors are all ≤ 1. The quantity $(r - s + c)/(2q + r + s + c)$, which is the ratio of polarizing relaxation transitions to the total relaxation rate, arises from both scalar (c) and dipolar (q, r, s) transition probabilities. Scalar and dipolar transition probabilities arise from transitions between the four spin states of the coupled spin system (Figure 1). The leakage factor $((T_B - T_1)/T_B)$ relates the bulk relaxation time (T_B) to that in the presence of radicals (T_1), and accounts for relaxation mechanisms other than those of interest here. Finally, the dependence of enhancement on applied radiofrequency power and the width of the epr line is accounted for by the electron saturation function, $S_e(P)$.

By extrapolating to infinite applied radiofrequency power ($S_e(P) \rightarrow 1$) and infinite radical concentration ($T_1 \rightarrow 0$), all systems are placed on a common scale and the appropriate relaxation mechanisms are isolated. Extrapolation gives the ultimate enhancement

$$U_\infty = \frac{\gamma_e}{\gamma_n} \frac{(r - s + c)}{(2q + r + s + c)} \quad (2)$$

At zero field,[4] dipolar transitions q, r, and s are in the ratio 3:2:12, while at higher fields, they may be estimated from proton enhancement measurements, since protons generally show no scalar coupling. At 74 G, the field of interest here, a reasonable estimate, obtained from such dipolar diffusion curves,[5] is $q/3.0 = r/1.6 = s/9.6$. Using these values and extrapolated enhancements, it is possible to calculate relative values of c for various systems and compare the scalar relaxation rate with the total dipolar rate.

Molecular motions in the system modulate the spin–spin interaction and induce the relaxation transitions. For this reason, q, r, s, and c depend on the nature of the collisional process. Theoretical treatments[6] based either on radical–solvent diffusion or molecular sticking lead to dipolar rates which depend principally upon the distance of closest approach d and the dipolar correlation time, τ_d. On the other hand, the scalar interaction is sensitive to spin density at magnetic nuclei and to the scalar correlation time τ_s, which need not be related to τ_d.[7] Both theories give

$$c = K\mathcal{A}^2\tau_s \quad (3)$$

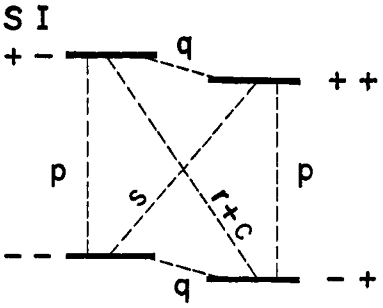

Figure 1. Energy levels and relaxation transitions for a coupled two-spin system, each of spin $^1/_2$.

where $\mathcal{A}$ is the hyperfine coupling constant. For ^{19}F nuclei, it was demonstrated experimentally[7] that as $\mathcal{A}$ increases, τ_s increases. This is also plausible for ^{31}P, because as the tendency for complexation increases (increase in τ_s), we would expect the relatively large electronic interactions between the radical and solvent to be reflected by increased hyperfine coupling. In the discussion to follow, we shall concentrate on mechanisms for scalar coupling by means of which collisional processes can be understood.

Experimental Section

Equipment. All measurements were performed at room temperature (24 ± 2°) in a magnetic field of 74 G. At this field, $\nu_H = 319.7$ kc, $\nu_P = 129.4$ kc, and $\nu_e = 210.7$ Mc. This sets the maximum limits for phosphorus nmr enhancement at -750 ($q = 3.0$, $r = 1.6$, $s = 9.6$, $c = 0$) and $+1620$ and ($c = \infty$). For the majority of samples, a 12-in. Varian iron-core magnet was used. However, in some cases, phosphorus zero signals were difficult to detect even after 1024 traces on a time-averaging computer. With these samples, the use of 4-ft diameter Helmholtz coils proved advantageous. A marginal oscillator was used for nmr detection, while a 100-W transmitter stimulated BDPA electron transitions. Phosphorus relaxation times for representative samples were measured by spin echoes at 3700 G. Epr spectra were obtained with a standard Varian X-band spectrometer.

Samples. BDPA was used exclusively to determine the effects of phosphorus environment because of its stability compared with other free radicals[8] which have been used for dynamic polarization measurements. A nominal radical concentration of 0.02 M was used for all samples. At this concentration, the width of the epr line was a function of the system; occasionally it was narrow enough to be saturated completely. Representative epr spectra of the two types are shown in Figure 2.

Because of these saturation difficulties, ultimate ^{31}P enhancements were evaluated by the ratio method[9] assuming -310 for $U_{\infty H}$. Thus, similar dipolar relaxation components were assumed for both ^1H and ^{31}P, and extrapolated proton enhancements which were removed from the dipolar limit were assumed to arise primarily from our inability to saturate the radical epr signal completely rather than from relaxation deficiencies. The epr spectra confirmed the reasonableness of this approach: all samples for which the extrapolated proton enhancement approached the dipolar limit gave a single, exchange-narrowed epr line, while those with more positive proton enhancements gave split signals. To apply the ratio method to phosphorus compounds which did not contain hydrogen, it was necessary to add 10% of a proton-containing solvent ($CHCl_3$ or C_6H_6). In addition, for several solid compounds ($(C_6H_5)_3PO$, $(C_6H_5)_3PS$, $(C_6H_5)_3P$, etc., saturated solutions in proton-containing solvents were used; this will be considered later when comparisons between systems are offered. Over-all, we estimate that ^1H enhancements are reproducible to ±10% and ^{31}P enhancements to ±15%.

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[4] I. Solomon, *Phys. Rev.*, **99**, 559 (1955).

[5] K. D. Kramer and W. Müller-Warmuth, *Z. Naturforsch.*, **19a** 375 (1964).

[6] P. S. Hubbard, *Proc. Roy. Soc.* (London), **A291**, 537 (1966).

[7] E. H. Poindexter, J. A. Potenza, D. D. Thompson, N. van Nghia, and R. H. Webb, *Mol. Phys.*, **14**, 385 (1968).

[8] E. H. Poindexter, J. R. Stewart, and P. J. Caplan, *J. Chem. Phys.*, **47**, 2862 (1967).

[9] J. R. Stewart, E. H. Poindexter, and J. A. Potenza, *J. Am. Chem. Soc.*, **89**, 6017 (1967).

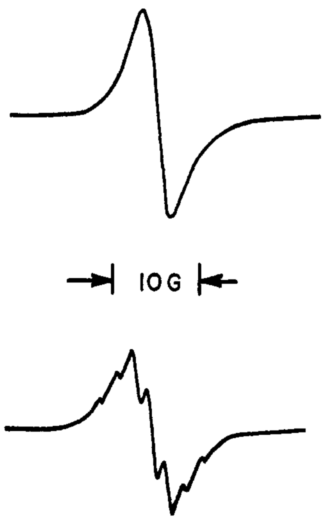

Figure 2. Representative epr spectra: (a) exchange narrowed; (b) not exchanged narrowed.

All phosphorus solvents were obtained commercially and used as received. Samples were deoxygenated by five freeze–pump–thaw cycles and sealed in glass.

Results

Experimental data for a variety of pentavalent, trivalent, and polyhedral phosphorus compounds are summarized in Tables I and II. There, $G_{100\text{H}}$ is the largest observed proton enhancement, $G_{\infty\text{H}}$ is the proton enhancement extrapolated to infinite radiofrequency power, while $G_{100\text{P}}$ and $G_{\infty\text{P}}$ are corresponding values for phosphorus in the same solutions. $U_{\infty\text{P}}$, the ultimate ^{31}P enhancement, was obtained from $G_{\infty\text{H}}$ and $G_{\infty\text{P}}$ by the ratio method. Finally, we list values for c_P, the ^{31}P contact relaxation component, obtained from eq 2.

Table I. Pentavalent Phosphorus

Solvent	$G_{100\text{H}}$	$G_{\infty\text{H}}$	$G_{100\text{P}}$	$G_{\infty\text{P}}$	$U_{\infty\text{P}}$	c_P
Phenylphosphonic Halides						
$(C_6H_5)_3PO/C_6H_8$	−140	−160	−270	−300	−590	1.3
$(C_6H_5)_2P(O)Cl$	−100	−115	−70	−90	−240	4.8
$C_6H_5P(O)Cl_2$	−115	−195	−2	−5	−8	7.9
$P(O)Cl_3/C_6H_6$	−185	−285	+550	+825	+895	39.1
$P(O)Br_3/C_6H_6$	−165	−280	+430	+600	+670	25.6
Phenylthiophosphonic Halides						
$(C_6H_5)_3PS/C_6H_6$	−190	−220	−350	−420	−600	1.2
$(C_6H_5)_3PS/CHCl_3$	−270	−320	−480	−550	−550	1.6
$(C_6H_5)PSCl_2$	−145	−230	+245	+370	+500	19.2
$P(S)Cl_3/C_6H_6$	−220	−310	+550	+705	+705	27.2
Alkyl and Thioalkyl Phosphates						
$(MeO)_3PO$	−135	−165	−310	−350	−650	0.8
$(EtO)_3PO$	−160	−210	−190	−280	−415	2.8
$(n\text{-}BuO)_3PO$	−105	−180	−195	−350	−595	1.2
$(C_6H_5O)_3PO/C_6H_6$	−140	−160	−270	−300	−590	1.2
$(EtO)_2P(O)Cl$	−75	−170	−80	−150	−280	4.3
$(EtO)_3PS$	−225	−330	−445	−580	−580	1.4
$(EtO)_2P(S)Cl$	−95	−275	−60	−90	−100	6.5
Dialkyl and Diaryl Phosphites						
$(MeO)_2P(H)O$	−110	−155	+40	+60	+125	10.1
$(EtO)_2P(H)O$	−190	−330	+30	+40	+40	8.6
$(n\text{-}BuO)_2P(H)O$	−115	−155	+30	+45	+90	9.4
$(C_6H_5O)_2P(H)O$	−95	−155	+95	+130	+260	12.8

Table II. Trivalent Phosphorus

Solvent	$G_{100\text{H}}$	$G_{\infty\text{H}}$	$G_{100\text{P}}$	$G_{\infty\text{P}}$	$U_{\infty\text{P}}$	c_P
Phenylphosphine Halides						
$(C_6H_5)_3P/C_6H_6$	−110	−150	+290	+415	+860	36.4
$(C_6H_5)_3P/CS_2$	−155	−255	+555	+800	+970	45.4
$(C_6H_5)_2PCl$	−125	−200	+480	+670	+1040	52.8
$C_6H_5PCl_2$	−200	−320	+665	+1090	+1090	59.4
PCl_3/C_6H_6	−190	−205	+870	+1070	+1610	∞
$C_6H_5PBr_2$	−135	−250	+460	+600	+745	29.3
PBr_3/C_6H_6	−200	−250	+870	+1050	+1300	109
Trialkyl Phosphites						
$(MeO)_3P$	−200	−310	+660	+1000	+1000	48.3
$(EtO)_3P$	−210	−330	+675	+950	+950	43.5
$(i\text{-}PrO)_3P$	−200	−290	+565	+775	+835	34.7
$(n\text{-}BuO)_3P$	−130	−230	+380	+605	+825	33.8
$(C_6H_5O)_3P/C_6H_6$	−240	−285	+795	+1000	+1050	54.1
Miscellaneous						
$(EtO)_2PCl$	−200	−310	+540	+790	+790	32.4
$(C_6H_5)_2PH$	−140	−155	+460	+525	+1060	55.4
Polyhedral Phosphorus						
$P_4/CS_2/C_6H_6$	−235	−285	+915	+970	+1050	54.1
$P_4S_3/CS_2/C_6H_6$	−280	−325	+1180	+1420	+1420	182

Phenylphosphonic Halides. The phenylphosphonic halides, $(C_6H_5)_nP(O)X_{3-n}$, provide a striking demonstration of the effect of halogen substitution at phosphorus. Contact components for P increase from 1.3 for $(C_6H_5)_3PO$ in benzene to 39.1 for $P(O)Cl_3$, while ultimate ^{31}P enhancements cover a range from −590 to +895. Also interesting is the observation that $P(O)Br_3$ shows considerably less scalar coupling than $P(O)Cl_3$.

Phenylthiophosphonic Halides. The phenylthiophosphonic halides show the same general trend as do their oxygenated analogs in that c_P increases with chlorination. However, the effect of substituting S for O is not clear; $C_6H_5P(S)Cl_2$ shows more scalar coupling than $C_6H_5P(O)Cl_2$, while for $P(S)Cl_3$ and $P(O)Cl_3$, the order is inverted.

Alkyl and Thioalkyl Phosphates. These compounds provide for further comparisons between O and S, again with results that support complex coupling effects. Hence, $(EtO)_3PS$ shows less scalar coupling than $(EtO)_3PO$, exactly the reverse of $(EtO)_2P(S)Cl$ and $(EtO)_2P(O)Cl$. By comparison, substitution of Cl for RO is straightforward: the effect of substituting Cl for RO is always to increase the degree of scalar coupling.

Dialkyl and Diaryl Phosphites. These compounds demonstrate the effect of H as a substituent. First, we note that all $(RO)_2P(H)O$ compounds are more positive than any corresponding alkyl- or thioalkyl phosphate, even those containing Cl substituents. In this regard, hydrogen, even though it is not expected to conjugate effectively with the central P atom, must be considered as a substituent which leads to large positive enhancements. No regular trend with increasing aliphatic chain length is noted; however, the aromatic phenyl group does lead to the most positive enhancement. Over-all, the major contribution to the enhancement appears to come from hydrogen, with the alkyl or aryl group acting as a small perturbation.

Phenylphosphine Halides. The phenylphosphine halides, $(C_6H_5)_nPCl_{3-n}$, are the first examples of trivalent P to be presented. We note that these compounds are all more positive than corresponding phenylphosphonic halides which contain pentavalent phosphorus. This effect is general; where direct comparisons are possible, no pentavalent compound yet has shown a more positive enhancement than the trivalent compound.[2,3a] Scalar coupling increases only slightly in the order $(C_6H_5)_3P < (C_6H_5)_2PCl < C_6H_5PCl_2$, whereas, for the phenylphosphonic halides, the effect of Cl substitution is much larger.

PCl_3 and PBr_3, although they should not be compared with the above compounds directly because of the added solvent, again show Br to be more negative than Cl. In addition, PCl_3 extrapolates, within experimental error, to the scalar limit, thus providing the largest degree of relative contact coupling ever observed in a nonmetallic fluid.

Trialkyl Phosphites. These compounds again show large positive enhancements indicative of trivalent phosphorus, and the contact component decreases regularly with chain length. Once again, phenyl shows a larger scalar rate than any R. Over-all, the trivalent oxidation state of P appears to set a polarization base line of about +700 which is then modified appropriately by the various substituents.

Polyhedral Phosphorus. Both white phosphorus, P_4, and P_4S_3 in CS_2 give large positive enhancements characteristic of trivalent phosphorus. With the exception of PCl_3, P_4S_3 gives the most positive enhancement observed. The relation of these enhancement parameters to those for other trivalent compounds is deferred to the following discussion.

General. We summarize the experimental observations thus: (1) trivalent P allows for more contact coupling than pentavalent P, (2) Br allows for less scalar coupling than Cl, (3) H allows for more scalar coupling than Cl, while Cl permits more scalar coupling than C_6H_5, (4) the effect of substituting S for O is strongly dependent on the system.

In the following discussion, we attempt to interpret these findings in terms of possible radical–solvent coupling mechanisms.

Discussion

From the above results, it is apparent that enhancement parameters for ^{31}P nuclei are extremely sensitive to the local environment of phosphorus. With just a single radical, $U_{\infty P}$ varies from almost the dipolar limit (−650 for $(MeO)_3PO$) to essentially the scalar limit (+1610 for PCl_3). Interestingly, some scalar coupling is observed in all cases. This large variation in contact coupling, which is more pronounced than that for fluorine nuclei in similar situations,[9] undoubtedly arises from the central location of P atoms in phosphorus compounds with consequent possibilities for substitution. Of course, fluorine and hydrogen atoms are located at molecular peripheries and should always be readily available for interaction with the free radical. Thus, phosphorus systems seem ideally suited to test for the presence of different types of coupling mechanisms, and questions as to how spin information is transmitted from the radical to both well-shielded and poorly shielded ^{31}P nuclei arise quite naturally.

Two mechanisms, each reflecting to some degree variations in a given parameter, have been used to interpret dynamic polarization results.[9,10] *Exchange polarization*[11] reflects the ability of the radical electron to unpair bonding electrons on the solvent and should primarily affect the isotropic hyperfine coupling constant $\mathcal{A}$, while tendencies toward *complexation* with concurrent charge transfer should be revealed most convincingly by measurement of the scalar correlation time τ_s. In the case of phosphorus, we make an additional distinction between intermolecular scalar coupling mechanisms. The exchange polarization process may be either *direct* or *indirect*, depending on whether the radical acts directly upon electrons situated at phosphorus, or indirectly *via* long-range conjugation. In an analogous way, charge transfer may be considered direct if the point of intermolecular contact is at phosphorus, or indirect if at some other atom. For fluorocarbons, molecular orbital calculations[10] showed that the highest spin density occurred at the point of contact, but, because of conjugation effects, the intramolecular solvent spin distribution was irregular with significant spin density at isolated sites. Qualitatively, differences in c_F, the contact component for fluorine, were interpreted in terms of different degrees of exchange polarization and complexation. We now examine the application of these concepts for the interpretation of ^{31}P enhancements.

Trivalent Phosphorus. Most likely, the large positive enhancements observed for trivalent P arise from the ability of the radical electron to correlate effectively with (unpair) the lone-pair electrons, leading to spin density at P. Since these electrons contain 3s character, the amount of which depends upon phosphorus hybridization, scalar components for all trivalent compounds are extremely large. However, since the lone-pair electrons should be readily available for complexation and since P atoms in trivalent phosphorus compounds are sterically available for direct coupling, it is impossible to say with certainty which mechanism predominates.

It may be that the observed order of enhancement for trivalent P reflects the amount of s character in the lone pair and hence phosphorus hybridization. This is a difficult conclusion to validate on the basis of our observations and the problem warrants further study. In particular, enhancements for the polyhedral species P_4 and P_3S_3, which are expected to maintain a rigid geometry[12] in solution, cannot be compared directly with other systems because of the added solvents. Further, bond angles obtained from X-ray studies of nonrigid trivalent compounds may not apply in solution. These complications aside, the striking positive effect of the lone-pair orbital is unequivocally demonstrated.

C_6H_5, Cl, and H Substituent Effects. The dramatic increase in enhancement with Cl substitution in the $(C_6H_5)_nP(O)X_{3-n}$ series may be attributed either to the small size of Cl as compared with a phenyl group or to the greater ability of Cl to conjugate with phosphorus and/or the radical *via* π bonding. That $P(O)Br_3$ gives a smaller enhancement than $P(O)Cl_3$ is in accord with both possibilities. However, phosphorus is well shielded in all directions by attached groups, and direct

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(10) J. A. Potenza and E. H. Poindexter, *J. Am. Chem. Soc.*, **90**, 6309 (1968).

(11) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

(12) J. R. Van Wazer, "Phosphorus and Its Compounds," Interscience Publishers, New York, N. Y., 1958.

coupling mechanisms between the free radical and P atoms seem unlikely. Indeed, since $U_{\infty P}$ for $P(O)Cl_3$ is more positive than that for several trivalent compounds, *strong* indirect coupling mechanisms resulting from exchange polarization and/or complexation at substituent sites are suggested.

Evidence for a direct coupling mechanism related to the distance of closest approach[3] comes from the dialkyl phosphites. As noted above, H directly bonded to P leads to relatively large scalar rates. Since H contains no available p or d orbitals, there is no *a priori* reason to expect it to promote strong complex formation. This leaves direct coupling of the radical with the electrons about P, which is highly favored because of the small size of H. We note, however, that conjugative mechanisms cannot be ruled out entirely.

The effect of long-range conjugation *via* the molecular system is demonstrated by $(C_6H_5O)_2P(H)O$ which shows a more positive enhancement than any dialkyl phosphite and by $(C_6H_5O)_3P$ which is more positively enhanced than any $(RO)_3P$. In particular, the phenyl group is larger than the methyl group, eliminating a predominant direct effect. A possible interpretation involves the greater ability of the aromatic system to transmit spin information to P *via* exchange polarization of or complexation with delocalized orbitals, in accord with previous interpretations for aromatic fluorocarbons.[10] If this is true, we might expect analogous variations in both $\mathcal{A}$ and τ_s.

Sulfur *vs.* **Oxygen.** Since sulfur is more polarizable than oxygen, we might expect thio-substituted compounds to show more scalar coupling than their oxygenated analogs if scalar coupling is transmitted through the molecular π system. Alternatively, a direct coupling mechanism would favor oxygen because it is smaller than sulfur. The experimental results, both for the phenylthiophosphonic halides and for the thioalkyl phosphites, show that neither possibility dominates and suggests the presence of competing mechanisms.

Concluding Remarks. If the lone-pair orbital is considered to be a substituent with a negligible steric effect, then, with the exception of sulfur and oxygen, the only two double-bonded substituents tested, ultimate enhancements decrease with increasing substituent size. In order of increasing polarization, $RO < C_6H_5 < Br < Cl < H <$ lone pair. This strongly suggests a scalar coupling process which includes unpairing of electrons directly bonded to phosphorus, even in compounds which are relatively well shielded sterically. On the other hand, long-range coupling *via* delocalized orbitals is required and may be the most important coupling process for some systems. The nature of these mechanisms, which incorporate variations in $\mathcal{A}$, τ_s, and d, should become more clear after additional measurements are performed. In particular, quantitative high-field measurements with several of these unusually stable systems would be of great value in determining the relative contributions of the various parameters.

Anisotropy of Fluorine Chemical Shifts in Substituted Fluorobenzenes

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Contribution from the Department of Chemistry, McGill University, Montreal, Quebec, Canada. *Received December 16, 1968*

Abstract: Fluorine chemical-shift anisotropies of some *para*-substituted fluorobenzenes have been determined in nematic liquid crystal solution. Changes in anisotropies relative to fluorobenzene have been correlated with Taft's inductive and resonance parameters. For fluorobenzene maximum shielding occurs along the axis perpendicular to the aromatic ring.

Various attempts have been made to calculate fluorine chemical shifts in aryl fluorides or to correlate calculated π-electron densities and π-bond orders with the observed isotropic shifts.[1-8] The analysis of magnetic resonance spectra of molecules dissolved in nematic liquid crystal solvents provides details of the anisotropy of the shielding tensor[9,10] which should, in principle, permit a further test of calculations of chemical shifts. The semiempirical theory of Karplus and Das[1] is attractive in this respect since it expresses the shielding in terms of localized bond parameters. This theory, and the extension by Prosser and Goodman,[2] demonstrated the importance of π charge densities in determining the fluorine chemical shift which has led to the correlation of the π densities with isotropic chemical shifts. Such approaches have been fairly successful providing no *ortho* substituents are present. The inclusion of long-range interactions produced a more satisfactory over-all correlation,[6] obviating the need for the "*ortho* effect," but the theoretical basis of the π-electron density calculations employed in this correlation has been questioned.[11]

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(1) M. Karplus and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961).

(2) F. Prosser and L. Goodman, *ibid.*, **38**, 374 (1963).

(3) R. W. Taft, F. Prosser, L. Goodman, and G. T. Davis, *ibid.*, **38**, 380 (1963).

(4) T. K. Wu and B. P. Dailey, *ibid.*, **41**, 2796 (1964).

(5) N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, **8**, 133 (1964).

(6) D. W. Davies, *ibid.*, 13, 465 (1967).

(7) J. W. Emsley, *J. Chem. Soc., A*, 2018 (1968).

(8) M. J. S. Dewar and J. Kelemen, *J. Chem. Phys.*, **49**, 499 (1968).

(9) A. D. Buckingham and K. A. McLauchlan, *Progr. NMR Spectry.*, 2, 63 (1967).

(10) A. Saupe, *Angew. Chem. Intern. Ed. Engl.*, **7**, 97 (1968).

(11) D. H. Lo and M. A. Whitehead, *Can. J. Chem.*, **46**, 2027 (1968).