$k_E = 10^{10.2}$ l./(mol sec), as reported.[6,19] To bring the values into agreement unilaterally would require that either $\Delta G°_{415}$ be in error by 1.4 kcal or that k_E be only $10^{8.7}$ l./(mol sec). This latter is improbably low but may be taken as a lower limit for the recombination of ethyl radicals. It suggests that the main source of disagreement is cumulative errors in the thermodynamic parameters.

The uncertainty in $\Delta G°_{415}$ is about ±1.6 kcal, which is well within the above limits and shows very good agreement between calculated and observed values. The chief contribution to these uncertainties in $\Delta G°$ are the heats of formation of the two radicals. The $\Delta H°_f$ and $S°$ values for MeI and EtI are much better known and have between them a combined uncertainty which amounts to less than 0.5 kcal contribution to $\Delta G°$.

Fessenden's reported values[7] for k_E obtained by direct esp measurement of Et· disappearance, albeit in liquid ethane, extrapolate to $10^{9.7}$ l./(mol sec) at 415°K. This yields a K_{ME} (kinetic) of 12, in substantially better agreement with the thermodynamic calculation.

Both Shepp and Kutschke[6] and Fessenden[7] report activation energies for Et· + Et· of 2.0 and 0.8 kcal/mol, respectively. While the present data have no bearing on this aspect, the desirability of further measurements at lower temperatures is indicated.

10% of the propane yields from which K_{ME} (kinetic) was determined. Furthermore, any such adjustments of this sort should also attempt to take into account propane and butane consumed during the course of reaction. That the effects of such side reactions are small and perhaps even self-compensating is evident from the invariance of K_{ME} (kinetic) with extent of reactions (Table I).

(19) Taking the average of the values at 50 and 100° in ref 6 and assuming that the recombination has no activation energy.

Steric Effects on Phosphorus Hyperfine Coupling Constants in Nitroaromatic Anion Radicals[1]

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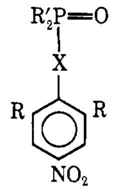
Abstract: Electron spin resonance spectra of the anion radicals produced by electrolytic reduction of 4-nitrophenyl diphenylphosphinate (I), 2,6-dimethyl-4-nitrophenyl diphenylphosphinate (II), 2,6-diphenyl-4-nitrophenyl diphenylphosphinate (III), *O,O*-diphenyl *S*-4-nitrophenyl thiophosphate (IV), and diethyl 2,6-dimethyl-4-nitrobenzylphosphonate (V) have been observed. The magnitude of the phosphorus hyperfine coupling constant, a_P, varied from 6.07 G for the anion radical obtained from I in acetonitrile to 27.15 G for the anion radical of IV in dimethylformamide. In the series of similar radicals I–III, a_P increases with increased bulk of the substituents in the 2 and 6 positions on the nitroaromatic ring. These data, in addition to comparison of data for V with data reported previously for its unmethylated analog, support the suggestion made previously that the magnitude of a_P contains an angular dependence similar to that found for proton hyperfine couplings when spin transmission occurs *via* hyperconjugation.

Stereochemical effects upon ^{31}P hyperfine coupling constants in nitroaromatic anion radicals have been of interest to us for some time. In a previous report[2] we described the electron spin resonance (esr) spectra of seven such radicals obtained by one electron reduction of phosphates and a phosphonate. We report now the extension of that work to a new series of nitroaromatic phosphorus anions derived from compounds I–V.

Our previous results[2] suggested that steric perturbations of the bonds linking the phosphorus atom to the nitroaromatic moiety (P–X–C) are important in determining the magnitude of the ^{31}P hyperfine interaction. The results reported now substantiate and elaborate this suggestion and provide sufficient data to permit some semiquantitative estimates of the parameters which describe a_P.



I, R = H; R′ = C_6H_5; X = O
II, R = CH_3; R′ = C_6H_5; X = O
III, R = C_6H_5; R′ = C_6H_5; X = O
IV, R = H; R′ = C_6H_5O; X = S
V, R = CH_3; R′ = C_2H_5O; X = CH_2

Experimental Section

Solvents for electrochemistry and tetraethylammonium perchlorate supporting electrolyte were commercially available and purified according to established literature procedures. Diphenyl chlorophosphate, diphenylphosphinic acid, triethyl phosphite, and 4-nitrothiophenol were obtained from Aldrich Chemical Co. Mucobromic acid, 1,3-diphenyl-2-propanone, triethylamine, and thionyl chloride were supplied by Eastman Organic Chemicals and 3-pentanone came from Matheson Coleman and Bell. 2,6-Dimethylbenzoic acid was obtained from K & K Laboratories.

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(1) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969. Address correspondence to the Department of Chemistry, Florida State University, Tallahassee, Fla.

(2) W. M. Gulick, Jr., and D. H. Geske, *J. Amer. Chem. Soc.*, **88**, 2928 (1966).

4-Nitrophenyl Diphenylphosphinate (I). A sample of this material was the gift of Professor Paul Haake and Dr. Gail Hurst[3] and was used as received.

2,6-Dimethyl-4-nitrophenyl Diphenylphosphinate (II). Sodium nitromalonaldehyde monohydrate was prepared by reaction of sodium nitrite and mucobromic acid as described by Fanta.[4] 2,6-Dimethyl-4-nitrophenol was obtained by condensation of 3-pentanone with the nitromalonaldehyde according to the method of Hill[5] as modified by Jones and Kenner.[6] Diphenylphosphinic chloride resulted from reaction of diphenylphosphinic acid with excess thionyl chloride. The product was isolated and purified by vacuum distillation. Reaction of equimolar quantities (27 mmol) of diphenylphosphinic chloride and 2,6-dimethyl-4-nitrophenol was carried out in acetone solution in the presence of approximately a 10% molar excess of triethylamine. Triethylamine hydrochloride was removed by filtration and vacuum evaporation of the solvent afforded crude II in high yield. The crude material was twice recrystallized from 95% ethanol. The resulting colorless to white crystals melted at 141–141.5°. We find no previous mention of this compound in the literature. The composition is established by elemental analysis. *Anal.* Calcd for $C_{20}H_{18}NO_4P$: C, 65.39; H, 4.94; N, 3.81; P, 8.43. Found:[7] C, 65.64; H, 4.97; N, 3.64; P, 8.70.

2,6-Diphenyl-4-nitrophenyl Diphenylphosphinate (III). 2,6-Diphenyl-4-nitrophenol was prepared from sodium nitromalonaldehyde monohydrate and 1,3-diphenyl-2-propanone as described by Hill.[5] Reaction of this phenol in acetone solution with an equimolar quantity of diphenylphosphinic chloride in the presence of triethylamine, as described for II, gave approximately 90% yield of crude III as a yellow semisolid. This crude product was dissolved in ether. The solution was extracted with two portions of distilled water, dried with $MgSO_4$, boiled briefly with decolorizing carbon, and filtered. Large, colorless crystals were obtained on cooling the ether solution. The product was recrystallized once more from ether. The resulting crystals contained ether which was removed by grinding the crystals to a fine powder and heating to 60° *in vacuo*. The resulting material melted at 158.5–159.5°. Since III appears to be a new compound, the composition is confirmed by elemental analysis. *Anal.* Calcd for $C_{30}H_{22}NO_4P$: C, 73.32; H, 4.48; N, 2.85; P, 6.31. Found:[7] C, 73.49; H, 4.62; N, 2.79; P, 6.42.

***O,O*-Diphenyl *S*-4-Nitrophenyl Thiophosphate (IV).** Reaction of diphenyl chlorophosphate and 4-nitrothiophenol in acetone solution in presence of excess triethylamine as described above afforded crude IV as a viscous oil upon removal of the solvent. This reaction did not proceed when ether was used as the reaction medium. The oil was dissolved in methanol. Slow evaporation of the methanol gave a pale brown solid which had an infrared spectrum consistent with the structure IV; in particular, the S–H stretching band was absent. Further recrystallization from alcohols failed; however pale yellow prisms were obtained by slow evaporation of a solution of IV in a mixture of 2 vol of hexane and 1 vol of chloroform. These crystals melted at 69.5–70.5°. We find no evidence of previous preparation of this compound. The composition is confirmed by elemental analysis. *Anal.* Calcd for $C_{18}H_{14}O_5NPS$: C, 55.81; H, 3.64; N, 3.61; P, 8.00; S, 8.28. Found:[8] C, 56.17; H, 3.65; N, 3.41; P, 7.98, 7.89; S, 8.50, 8.39.

Diethyl 2,6-Dimethyl-4-nitrobenzylphosphonate (V). 2,6-Dimethylbenzoic acid was reduced with $LiAlH_4$ as described by Raaen and Eastham[9] to produce the benzyl alcohol. Treatment of the alcohol with thionyl chloride yielded 2,6-dimethylbenzyl chloride,[9] bp 55° (0.1 mm). Reaction of 10 g (64 mmol) of the benzyl chloride with excess triethyl phosphite according to the method of Kagan, *et al.*,[10] produced a nearly quantitative yield of diethyl 2,6-dimethylbenzylphosphonate, bp 110° (0.1 mm). The composition was established *via* infrared spectroscopy and high-resolution mass spectroscopy: molecular ion *m/e* 256.1225 (calcd for $C_{13}H_{21}O_3P$, 256.1228). Nitration was carried out using a slight modification of the procedure used by Kosolapoff[11] for nitration of di-*n*-butyl benzylphosphonate. Diethyl 2,6-dimethylbenzylphosphonate (8.45 g, 33 mmol) was added dropwide to an ice-cold mixture of 8 ml of concentrated H_2SO_4 and 4 ml of concentrated HNO_3. After 40 min the reaction mixture was poured onto ice, washed with aqueous Na_2CO_3, extracted into benzene, and distilled *in vacuo*. Approximately 2 g of crude V was obtained as a viscous yellow liquid, bp 185° (0.1 mm). Mass spectroscopy showed that this product contained approximately 20% dinitrophosphonate, molecular ion *m/e* 346.0932 (calcd for $C_{13}H_{19}N_2O_7P$, 346.0928), as well as the desired mononitro compound, molecular ion *m/e* 301.1065 (calcd for $C_{13}H_{20}NO_5P$, 301.1078). Thin layer chromatography on silica gel GF revealed at least five components when eluted with a mixture of ethyl acetate–10% absolute ethanol. The major spot proved to contain (mass spectroscopy) both the mono- and dinitro materials.

The entire sample was subjected to preparative tlc with recovery of the major spot. The partially purified material was chromatographed (also on silica gel GF) using the continuous elution technique[12] employing ethyl acetate–10% benzene. This approach afforded resolution of the two components, the dinitro compound exhibiting the larger R_f value. V was isolated as required by leeching from tlc plates. *Anal.* Calcd for $C_{13}H_{20}O_5PN$: C, 51.82; H, 6.69; N, 4.64; P, 10.28. Found:[7] C, 51.82; H, 6.42; N, 4.85; P, 10.15.

Electron Spin Resonance. Esr experiments at Cornell University were carried out using the Varian V-4500 spectrometer system and the field-sweep calibration technique described previously.[13,14] At Florida State University, esr measurements were made with a Varian E-12 spectrometer; the field sweep was calibrated with Fremi's salt in aqueous sodium carbonate solution. All the free radicals reported here were generated by electrolytic reduction at 25° using the *intra muros*[15] technique. Assignments of coupling constants have been confirmed by comparison of the experimental spectra with spectra calculated using a slightly modified version of the computer program devised by Stone and Maki.[16] This program was executed on an IBM 360-65 computer at Cornell and on a CDC 6400 computer at Florida State University.

Polarography. Polarographic measurements at Cornell were made using the ORNL three-electrode polarograph described previously.[13] A three-electrode polarograph constructed in our laboratory using all solid state Philbrick operational amplifiers and the Kelly–Fisher–Jones[17] current amplifier configuration was employed at Florida State University. All experiments were performed at approximately 25° and we report maximum, not average, diffusion currents. Potential measurements were made *vs.* the aqueous saturated calomel electrode under conditions of "long immersion;"[18] the precision of these measurements is believed to be ±5 mV. In all electrochemical procedures, tetraethylammonium perchlorate at 0.1 *M* concentration was employed as supporting electrolyte.

Results

Polarography. Compounds I–V exhibited reproducible polarographic reduction waves which yielded the electrochemical parameters given in Table I. These results represent average values from at least three polarograms for each compound.

Esr. *Intra muros* electroreduction of solutions *ca.* 1 m*M* in compounds I–V in both acetonitrile and dimethylformamide (DMF) produced strong esr signals which were attributable to the corresponding anion radicals. Esr data are summarized in Table II where we report average values of coupling constants obtained from the high- and low-field branches of two or more spectra.

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(3) P. Haake and G. Hurst, *J. Amer. Chem. Soc.*, **88**, 2544 (1966).

(4) P. Fanta, *Org. Syn.*, **32**, 95 (1952).

(5) H. B. Hill, *Amer. Chem. J.*, **24**, 1 (1900).

(6) E. Jones and J. Kenner, *J. Chem. Soc.*, 1842 (1931).

(7) Galbraith Laboratories, Knoxville, Tenn.

(8) Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(9) V. F. Raaen and J. F. Eastham, *J. Amer. Chem. Soc.*, **82**, 1349 (1960).

(10) F. Kagan, R. D. Birkenmeyer, and R. E. Strube, *ibid.*, **81**, 3026 (1959).

(11) G. M. Kosolapoff, *ibid.*, **71**, 1876 (1949).

(12) E. Stahl, "Thin Layer Chromatography," M. R. F. Ashworth, translator, Springer-Verlag, New York, N. Y., 1969, p 69.

(13) K. Kuwata and D. H. Geske, *J. Amer. Chem. Soc.*, **86**, 2101 (1964).

(14) W. M. Gulick, Jr., and D. H. Geske, *ibid.*, **88**, 4119 (1966).

(15) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **30**, 1356 (1961).

(16) E. W. Stone and A. H. Maki, *ibid.*, **38**, 1999 (1963).

(17) M. T. Kelley, H. C. Jones, and D. J. Fisher, *Anal. Chem.*, **31**, 1475 (1959).

(18) D. H. Geske, J. L. Ragle, M. Bambenek, and A. L. Balch, *J. Amer. Chem. Soc.*, **86**, 987 (1964).

Table I. Polarographic Results in Acetonitrile

Compd	$-E_{1/2}$, V	$-(E_{3/4} - E_{1/4})$, mV	i_d/C, μA mM^{-1}
I	1.15_3	56	4.39
II	1.18_0	54	3.84
III	1.08_6	51	4.06
IV	1.00_9	60	~2.5[a]
V	1.28_0	57	4.35
Nitrobenzene[b]	1.14_7	56	

[a] Measurement complicated by apparent adsorption effect which leads to unusually short drop times (~1.5 sec as compared with ~6 sec for the other compounds). [b] Data from ref 18.

Table II. Electron Spin Resonance Data[a]

Anion radical		Acetonitrile	DMF
I	a_N	10.40 ± 0.06	9.88 ± 0.07
	$a_{H(o)}$	3.43 ± 0.07	3.46 ± 0.05
	$a_{H(m)}$	1.12 ± 0.02	1.12 ± 0.01
	a_P	6.07 ± 0.06	6.35 ± 0.08
II	a_N	10.58 ± 0.05	10.00 ± 0.04
	$a_{H(o)}$	3.36 ± 0.01	3.37 ± 0.02
	a_{CH_3}	1.04 ± 0.01	1.04 ± 0.01
	a_P	9.32 ± 0.06	9.66 ± 0.04
III	a_N	10.00 ± 0.06	9.53 ± 0.03
	$a_{H(o)}$	3.35 ± 0.01	3.33 ± 0.02
	a_P	10.00 ± 0.06	10.49 ± 0.04
IV	a_N	8.48 ± 0.05	7.78 ± 0.03
	$a_{H(o)}$	3.28 ± 0.01	3.23 ± 0.01
	$a_{H(m)}$	0.96 ± 0.02	0.90 ± 0.01
	a_P	24.80 ± 0.11	27.15 ± 0.11
V	a_N	11.06 ± 0.05	10.29 ± 0.06
	$a_{H(o)}$	3.33 ± 0.03	3.36 ± 0.02
	a_{CH_3}	1.04 ± 0.02	1.01 ± 0.02
	a_{CH_2}	2.29 ± 0.02	2.34 ± 0.01
	a_P	19.14 ± 0.07	20.09 ± 0.07
Nitrobenzene[b]	a_N	10.32	9.83
	$a_{H(o)}$	3.39	3.32
	$a_{H(m)}$	1.09	1.09
	$a_{H(p)}$	3.97	3.97

[a] Absolute values of coupling constants in gauss with uncertainties given at the 95% confidence level. Proton positions are indicated with respect to the nitro group. While g values were not determined exactly, all the radicals had $g \sim 2.0$. [b] Acetonitrile data from D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, **82**, 2671 (1960); DMF data from P. Ludwig, T. Layloff, and R. N. Adams, *ibid.*, **86**, 4568 (1964).

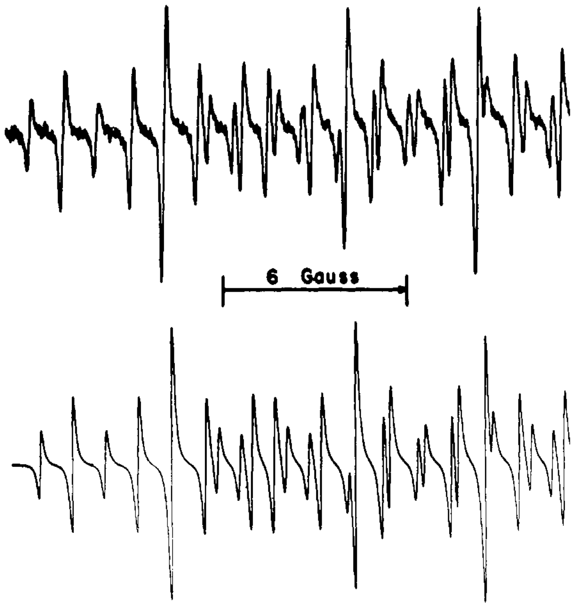

Figure 1. Upper trace: low-field half of the esr spectrum of radical I obtained by electroreduction of an acetonitrile solution 0.7 mmol in compound I. Lower trace: computed spectrum using $a_N = 10.27$, $a_H = 3.35$, $a_H = 1.12$, $a_P = 6.02$, and line width = 0.125 G with Lorentzian line shape.

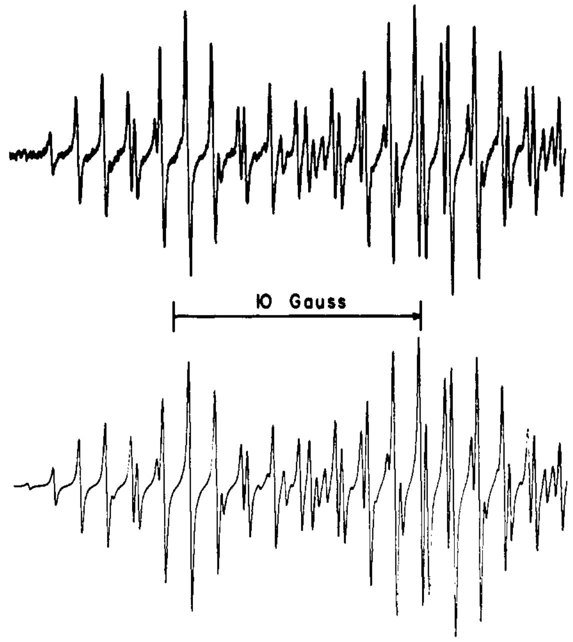

Figure 2. Upper trace: low-field half of the esr spectrum of radical II obtained by electroreducton of an acetonitrile solution 0.8 mmol in compound II. Lower trace: computed spectrum using $a_N = 10.55$, $a_H = 3.365$, $a_{CH_3} = 1.04$, $a_P = 9.24$, and line width = 0.120 G with Lorentzian line shape.

Figures 1–3 compare the experimental spectra of radicals I, II, and V in acetonitrile solution with computed spectra. Comparable agreement was obtained for spectra in DMF solution. The computed spectra were obtained using the coupling constants measured from the individual spectra presented in the figures and those values are given in the figure captions. This procedure was necessitated by small variations in coupling constants among replicate spectra, a phenomenon reflected in the uncertainties quoted in Table II.

Assignment of spectra for radicals III and IV was straightforward and these spectra are omitted for brevity. For radical III in DMF all 18 lines are observable, whereas in acetonitrile this number is reduced to 12 by the accidental equivalence of a_N and a_P. Computed spectra indicate that the equivalence of these coupling constants is at a level well within the uncertainty of the measurements. Although no interactions with the protons of the *m*-phenyl groups were resolvable, such interactions probably account for the large line widths (0.34 G) observed in spectra of III. The very large phosphorus coupling constant for radical IV permitted unique resolution of all 54 hyperfine lines when the solvent was DMF. In acetonitrile solution a small number of overlaps occurred, but assignment of the spectrum was still unambiguous.

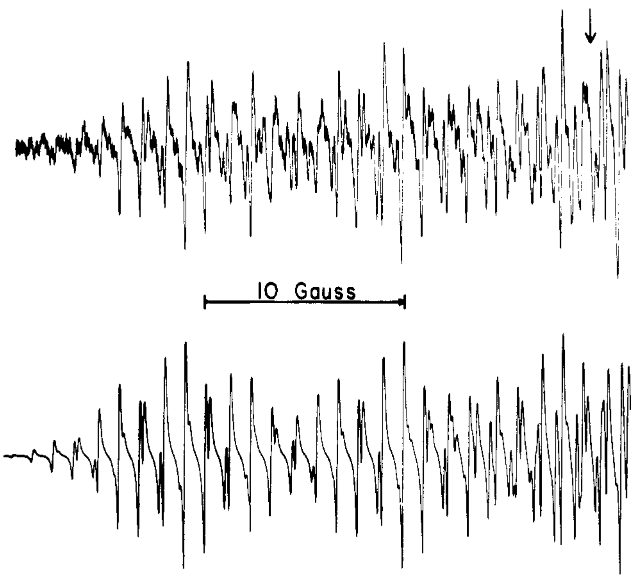

Figure 3. Upper trace: low-field section of the esr spectrum of radical V obtained by electroreduction of an acetonitrile solution 1.5 mmol in compound V. Slightly more than half the spectrum is shown; the arrow indicates the center. Lower trace: computed spectrum using the coupling constants given in Table II, line width = 0.130 G, and Lorentzian line shape. Due to the large number of overlapped lines, these computations were very sensitive to small (10–50 mG) changes in the two largest coupling constants.

Discussion

Our previous investigation[2] led us to suggest tentatively that electron spin density is transmitted from the nitrophenyl ring to the substituent phosphorus atom *via* a hyperconjugation-like mechanism. Direct interaction of orbitals on phosphorus with the p_z orbital of the C_4 carbon atom in the aromatic ring would be required for such a mechanism. The spin density on phosphorus, and therefore the magnitude of the ^{31}P hyperfine interaction, would be expected to depend upon the physical proximity of the phosphorus atom to this orbital.

It is well established[19] that for proton coupling constants in fragments of the form $XCH_2\dot{C}H_2$ the β-proton coupling constant is expressible by eq 1. Here B and B_0

$$a_H = (B_0 + B\langle\cos^2\theta\rangle)\rho^\pi \qquad (1)$$

are constants with $B \gg B_0$ and θ is the angle between the C–H bond and the axis of the p_z orbital associated with the paramagnetic center both projected on a plane perpendicular to the carbon–carbon bond. ρ^π is the spin density at the α position.

In analogy to this treatment, we suggested the possibility of a relation such as eq 2 to describe ^{31}P hyper-

$$a_P = C\langle\cos^2\theta\rangle\rho_{C_4}^\pi \qquad (2)$$

fine splittings in a series of similar nitroaromatic phosphorus radicals.[2] Here θ is the angle between the axis of the p_z orbital on C_4 of the nitroaromatic ring and the P–X bond, both projected on a plane perpendicular to the X–C_4 bond. This suggestion was based primarily on the observations that in acetonitrile a_P was 7.92 G in diphenyl 4-nitrophenylphosphate (4 in ref 2; R = H, R′ = C_6H_5O, X = O in the present nomenclature) and 10.50 G in diphenyl 2,6-dimethyl-4-nitrophenyl phosphate (5 in ref 2; R = CH_3, R′ = C_6H_5O, X = O) and further, that in diethyl 4-nitrobenzylphosphonate (3 in ref 2; R = H, R′ = C_2H_5O, X = CH_2) the proton splitting for the bridging methylene group (2.70 G) was considerably smaller than that found in 4-nitrotoluene, 3.98 G. We felt that the first pair of observations implied a decrease in the angle θ, and the second indicated that since the phosphorus atom was sterically held away from the plane of the nitrophenyl ring (small θ) the steric environment of the methylene protons was constrained to be unfavorable for hyperconjugation. The mechanistic interpretation was of necessity tentative; in the first case we did not know with certainty the inductive effect at ^{31}P of 3,5-dimethylation of the aromatic ring, while in the second we did not know the nature of the inductive effect to be expected from replacing one proton in 4-nitrotoluene with $(C_2H_5O)_2P(O)$–.

The implication of eq 2 is that if, in a series of otherwise similar radicals, one goes from a situation in which there is free rotation of phosphorus about the X–C bond to a situation in which steric hindrance constrains $\theta \sim 0°$, the magnitude of a_P should double (the value of $\cos^2\theta$ averaged over all values of θ is 0.5). As can be seen in Table II, this is approximately the case for the series I–III; a_P increases from *ca.* 6 G in the unhindered radical I to *ca.* 10 G in III. The data for this series are more complete than any previous data since we were able to prepare radicals in which both electron-releasing and electron-withdrawing groups were responsible for the steric perturbation. In accord with the stereochemical hypothesis, a_P continues to increase from II to III as the size of the blocking group increases, despite their different inductive properties.

Comparison of the nitrogen and ring proton coupling constants as well as the reduction potential for I with values for nitrobenzene suggests strongly that the $(C_6H_5)_2P(O)O$– substituent has a negligible effect upon the electronic structure of the nitroaromatic ring. Differences observed between these same parameters in II and III and in nitrobenzene are such that they can be rationalized on the basis of effects anticipated[18,20] for the meta hydrocarbon substituents. Thus, since the necessary parameters for the phosphorus substituent are not well established, we feel that an *estimate* of the spin density at C_4 can reasonably be obtained from molecular orbital calculations for the corresponding meta-substituted nitrobenzene anions. Results of Hückel calculations employing the McLachlan[21] approximate configuration interaction method are given in Table III. Using these values of $\rho_{C_4}^\pi$ we can proceed to estimate, albeit relatively crudely, values of C in eq 2.

The fact that the increase in a_P noted from I to III is less than twofold may be explained in several ways which may contribute in unknown proportions. The phosphorus group may not be entirely free to rotate in I, and/or residual torsional motions in III may prevent $\langle\cos^2\theta\rangle$ from reaching its limiting value of unity. In addition, there may exist a spin polarization term analogous to B_0 in eq 1 which is independent of θ.

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[19] R. Bersohn, *J. Chem. Phys.*, **24**, 1066 (1956); E. W. Stone and A. H. Maki, *ibid.*, **37**, 1326 (1962); **38**, 1254 (1963).

[20] A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, **83**, 1852 (1961).

[21] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

Table III. Molecular Orbital Calculations

Radical anion[a]	Spin densities N	O	C_1	C_2	C_3	C_4
Nitrobenzene	0.247	0.198	0.001	0.142	−0.049	0.168
3,5-Dimethylnitrobenzene[b]	0.247	0.198	0.001	0.144	−0.047	0.169
3,5-Diphenylnitrobenzene[c]	0.245	0.196	0.002	0.143	−0.047	0.175
3,4,5-Trimethylnitrobenzene[b]	0.246	0.196	0.001	0.142	−0.046	0.163

[a] Calculations performed on hydrocarbon substituted nitrobenzene anion radicals to estimate spin densities in the absence of established MO parameters for the phosphorus substituents; data here indicate little electronic perturbation on the nitroaromatic ring from these substituents (see text). MO parameters are those for acetonitrile solution from P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963). [b] Methyl groups included using parameters suggested by C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953). [c] On the basis of molecular models, we estimate that the *m*-phenyl groups make an angle of about 60° with the nitrophenyl group and have employed a resonance integral appropriate for this angle.

Thus, we might wish to formulate the phosphorus coupling constant as in eq 3. An upper limit to the

$$a_P = (C_0 + C\langle\cos^2\theta\rangle)\rho_{C_4}^{\pi} \qquad (3)$$

contribution of C_0 may be determined by assuming that $\langle\cos^2\theta\rangle$ has the values 0.5 and 1.0 respectively in I and III. Using the acetonitrile data for I and III and the calculated spin densities with these assumptions, one obtains C_0 = 15.5 G and C = 41.6 G.

Examination of space-filling molecular models, however, suggests that in I there is considerable steric hindrance of conformations in which the phosphorus atom lies in the plane of the nitroaromatic moiety. Hence, of the two assumptions above, the more realistic one is $\langle\cos^2\theta\rangle = 1$ in radical III. If we ascribe the entire discrepancy between our data and the expected twofold increase in a_P to steric hindrance in I (*i.e.*, $C_0 = 0$), then a value of C = 56 G is obtained. It seems certain that C_0 is less than 15.5 G and very likely that a hyperconjugative term with $C \sim 50$ G dominates the behavior of a_P in the series of radicals I–III.

Radical V provides the most convincing evidence supporting our assertion of the importance of steric effects. In the unmethylated analog (3, ref 2; *vide supra*) we found $a_P = 13.59 \pm 0.23$ G in acetonitrile and 17.51 ± 0.24 G in DMF, while the corresponding values of a_{CH_2} were 2.70 ± 0.02 and 2.81 ± 0.02 G. Comparison of these data with results for radical V (Table II) shows that in both solvents introduction of the *m*-methyl groups leads to a substantial increase in a_P and a *decrease* in a_{CH_2} well outside the limits of uncertainty in the coupling constants. Barring the unlikely circumstance that spin transmission to phosphorus involves some through space interaction with another part of the nitroaromatic ring, both a_P and a_{CH_2} depend upon the same spin density, $\rho_{C_4}^{\pi}$. Thus, the changes of these coupling constants in opposite directions appear to prove the assertion of a steric effect; as conformations in which the phosphorus atom occupies positions for which $\theta \sim 0°$ become preferred, the methylene protons are forced to occupy positions for which $\theta \sim 60°$. We presume that radicals of this type have a larger phosphorus splitting than those in which the bridging atom, X, is oxygen, at least in part because of the more acute[2] P–CH$_2$–C angle (109° *vs.* 120°).

In analogy to the procedure followed for radicals I–III, we obtain a rough estimate of $\rho_{C_4}^{\pi}$ in V by noting that a_N and $E_{1/2}$ are closely similar to values found in 3,4-dimethylnitrobenzene anion[18] and therefore simulate V with an MO calculation for 3,4,5-trimethylnitrobenzene anion (Table III). On this basis (assuming $C_0 = 0$), a preliminary estimate of C for phosphonate radicals is 115 G.

Radical IV is the first case in the 12 organophosphorus radicals studied here and in ref 2 in which we observe a substantial difference in spin density distribution from unsubstituted nitrobenzene anion. The most evident result of this electronic effect is a reduction of a_N by ∼20% from the value observed in nitrobenzene anion; ring proton splittings are also diminished slightly. The inductive effect of the substituent thiophosphate group is also reflected in the reduction potential for IV which is the most anodic of any of the organophosphorus free radicals we have studied in acetonitrile. Comparison of data for radical IV with those of the anion radical of 4-nitrobenzamide[20] suggests that the electronic effects of $-C(O)NH_2$ and $-SP(O)(OC_6H_5)_2$ are exceedingly similar. Maki and Geske found a_N = 8.37 G, $a_{H(o)}$ = 3.20 G, $a_{H(m)}$ = 0.98 G, and $E_{1/2}$ = −1.014 V in the former case.

It is interesting to note that both the electronic effects discussed in the preceding paragraph and the very large ^{31}P splitting observed for IV are specific effects of substitution of sulfur for oxygen *at the bridging position*. Radical IV is closely related to the parathion anion radical (*O,O*-diethyl *O*-4-nitrophenyl thiophosphate anion) reported in ref 2 for which the coupling constants in acetonitrile were a_N = 10.27, $a_{H(o)}$ = 3.47, $a_{H(m)}$ = 1.13, a_P = 10.29. Other previous data[2] showed that a_P was substantially the same in radicals containing ethyl and phenyl ester groups, so we attribute the increase in a_P primarily to the movement of the sulfur atom from the phosphoryl position to the bridge position. The marked increase in the ^{31}P interaction could be the result of a combination of increased conjugation through sulfur (the possibility of d-orbital participation exists) and also a geometrical factor since the P–S–C angle is likely to be more acute[22] than the value of 120° observed[23] for P–O–C. An X-ray crystallographic study of IV is in progress to investigate this latter point.

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(22) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 110; F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, pp 393, 394.

(23) W. O. Davies and E. Stanley, *Acta Crystallogr.*, **15**, 1092 (1962).

facilities through Grant GU-2612 to Florida State University. NIH support of the mass spectrometry facilities at Cornell University is acknowledged. We thank Miss Vicki J. King for valuable technical assistance and Professor Paul Haake and Dr. Gail Hurst for a gift of compound I.

Solvent and Temperature Dependence of Hydrogen–Hydrogen, Hydrogen–Fluorine, and Fluorine–Fluorine Coupling Constants in Difluoroethylenes[1]

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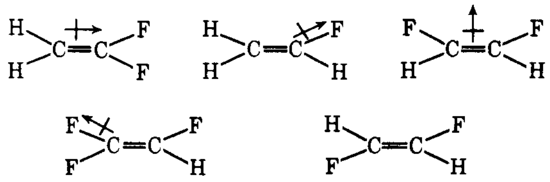
Abstract: Solvent- and temperature-induced variations of H–H, H–F, and F–F coupling constants in *cis*- and *trans*-1,2-difluoroethylene and 1,1-difluoroethylene are reported. These data, in conjunction with previous results, confirm that orientation of the solute dipole affects the magnitude of the solvent effect on geminal H–H and H–F coupling constants. Dipole orientation is not a factor in determining solvent effects on vicinal H–F and F–F coupling constants. The changes observed for vicinal H–F coupling constants are proportional to $\sqrt{^3J_{HF}}$. The dipole-induced solvent electric field is the primary causative factor producing the observed changes, but dispersion forces and specific interactions are also important. The best fit for a regression analysis of coupling constants against solvent parameters is of the form $J_{obsd} = J_0 + AR + BD$, where R and D represent reaction field and dispersion field terms. A and B are opposite in sign. Rough values of ΔH and ΔS are reported for weak solute–solvent complexes characterizing specific interactions effects. An apparent dichotomy is reported where one coupling constant in a molecule is solvent dependent but another is not, even though the same nuclei are involved in both couplings.

Solvent-induced variations of various coupling constants ranging from 0.30 Hz to 10.0 Hz have been reported in several hundred compounds.[2] The properties of the solute molecule and the solute–solvent interactions conducive to solvent-dependent coupling constants are the subject of much speculation. For the limited case of geminal H–H coupling constants, previous investigations[3,5] have implicated the solute dipole as a necessary condition for solvent dependency. The observation that $^2J_{HF}$ of vinyl fluoride increases while $^2J_{HF}$ of trifluoroethylene decreases under similar conditions confirmed that the solvent effect depends on the presence of the solute dipole, and on its orientation.[4] In these cases it is assumed that the dipole-induced solvent electric field (reaction field) alters the electronic distribution of the solute molecule, resulting in the observed changes in geminal coupling constants. However, reaction field effects are not the only mode of solute–solvent interaction. Laszlo[6] has demonstrated an excellent correlation between dispersion forces and coupling constant changes in symmetric molecules. Recently, Goldstein[7] has developed and tested a model involving both reaction field terms and equilibrium constants for collision complexes in order to explain discrepancies in extrapolating reaction field terms to high dielectric constant solvents. The difluoroethylenes provide a number of unique opportunities to clarify some of these problems.

The cis isomer possesses a permanent dipole whose orientation relative to the H–C–F group is intermediate to that of vinyl fluoride and trifluoroethylene, while the trans isomer contains the same H–C–F group but has no dipole moment. The dipole moment–solvent electric field concept predicts that ΔJ_{max}[8] for *cis*-1,2-difluoroethylene should be between the values observed for vinyl fluoride and trifluoroethylene, while $^2J_{HF}$ of *trans*-1,2-difluoroethylene should be solvent invariant.



All three isomers have a nice array of vicinal H–F couplings. Previous studies[4,9] indicate that solvent effects on vicinal H–F coupling constants are at least an order of magnitude larger than solvent effects on the corresponding vicinal H–H couplings (which are generally insensitive to solvent). The 1,2-difluoroethylenes present an excellent opportunity to compare the solvent-induced changes of vicinal H–F coupling constants with the corresponding changes in geminal

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[2] References 3 and 4 contain many citations for early reports of solvent-dependent coupling constants.

[3] S. L. Smith and R. H. Cox, *J. Chem. Phys.*, **45**, 2848 (1966).

[4] S. L. Smith and A. M. Ihrig, *ibid.*, **46**, 1181 (1967).

[5] V. S. Watts and J. H. Goldstein, *ibid.*, **42**, 228 (1965).

[6] P. Laszio and A. Speert, *J. Magn. Resonance*, **1**, 291 (1969).

[7] R. L. Schmidt, R. S. Buttler, and J. H. Goldstein, *J. Phys. Chem.*, **73**, 1117 (1969).

[8] A positive ΔJ is defined as a change for which J increases algebraically with enhanced solvent polarity.

[9] H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **45**, 1111 (1967).