Influence of Protonic Solvents on Spin–Spin Coupling involving Phosphorus directly Bonded to Hydrogen, Fluorine, or Another Phosphorus Atom in Phosphoryl and Thiophosphoryl Molecules

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The effect on the n.m.r. spectral parameters of dissolving five different phosphoryl and thiophosphoryl compounds in a series of organic solvents of varying protonic acidity was studied. For all five of these compounds, the absolute magnitudes of the coupling constants for the directly bonded magnetically active nuclei increased with solvent acidity, whilst there was also a concurrent small change in the chemical shift(s). These and related results are discussed in terms of association with the acidic solvent through hydrogen bonding at the phosphoryl oxygen atom (or thiophosphoryl sulphur atom). Some pertinent semi-empirical LCAO–MO–SCF calculations have been carried out for these molecules, with and without hydrogen bonding.

ALTHOUGH there is considerable literature [1-4] on the effect of solvents on n.m.r. coupling constants and chemical shifts, there are few papers [5-13] on this topic for un-ionized phosphorus compounds, and some of these [10-13] are confined to the necessarily small effects found in spin–spin coupling between the phosphorus and a hydrogen atom separated by one or two intermediate atoms. An important feature of all of the literature dealing with n.m.r. solvent effects is the influence of solvent–solute association (as in hydrogen bonding) on the spin–spin coupling between directly bonded magnetically active nuclei.

We have considered the effect of hydrogen bonding between a protonic solvent and the phosphoryl oxygen atom (or thiophosphoryl sulphur atom) of compounds in which either a hydrogen, a fluorine, or another phosphorus atom is directly bonded to the phosphoryl (and also in the case of the hydrogen only, a thiophosphoryl) phosphorus atom.

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[1] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1955, ch. 12.

[2] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High-Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, Oxford, vol. 2.

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EXPERIMENTAL

Commercial dimethyl phosphonate and diethyl phosphonate (Aldrich) were distilled before use. Diethyl phosphorofluoridate was obtained by chlorinolysis of diethyl phosphonate with sulphuryl chloride, followed by exchange with sodium fluoride in benzene solution,[14] and had b.p. 60—62° at 12 mmHg. Dimethyl thiophosphonate was prepared by reaction of dimethyl phosphorochloridite with hydrogen sulphide in the presence of pyridine,[15] and had b.p. 51—52° at 12 mmHg. Tetraethyl monothiohypophosphate was obtained according to J. Michalski *et al.*[16] The chosen fraction, distilled at 90—93° and 0·05 mmHg, contained *ca.* 20% *sym*-tetraethyl dithiohypophosphate which could not be removed by vacuum distillation. The identity of the compounds used was proven by ^{31}P n.m.r. spectroscopy as well as with a LKB Gas-Chromatograph Mass-Spectrometer 9000.

The ^{1}H n.m.r. data were recorded on Varian A-60 and XL-100-15 spectrometers. The XL-100-15, using a 15 in magnet and the frequency-sweep mode, was operated at 23,490 gauss for ^{1}H, ^{19}F, and ^{31}P (100·0, 94·1, and 40·5 Hz respectively). In all cases, this spectrometer was locked on the deuterium resonance of [$^{2}H_6$]acetone (15·4 MHz) contained in a 12 mm o.d. tube along with an appropriate ' external ' reference [Me_4Si, $CFCl_3$, or $(PhO)_3P$]. Teflon spacers ensured that the sample for analysis contained in a 5 mm o.d. tube remained centrally located in the 12 mm tube while spinning. When desirable, the ^{1}H frequencies were noise-decoupled (110 dB at 10,000 Hz width) to give a sharp singlet in the ^{31}P spectrum. All chemical shifts are reported with reference to neat Me_4Si for ^{1}H, neat $CFCl_3$ for ^{19}F, and 85% H_3PO_4 for ^{31}P, with downfield shifts being negative.

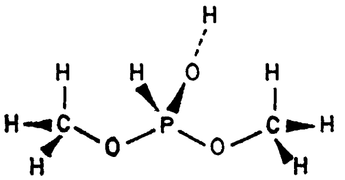

FIGURE 1 Geometrical arrangement used in the SCF calculation of the interaction between a proton and the phosphoryl oxygen of dimethyl phosphonate. Various $H^+ \cdots O$ distances were tested along the line connecting the phosphorus, oxygen, and proton

The SCF computations[17] were carried out by use of CNDO.[18] Three different molecular cases were treated. For the first, the dimethyl phosphonate molecule was oriented in the stretched-out configuration shown in Figure 1; a proton was positioned at various distances from the phosphoryl oxygen along the P=O bond axis so that the sequence of atoms HCOPOCH lay in the same plane. In the second molecular case, the hydrogen of a formic acid molecule was brought towards the phosphoryl oxygen atom of the dimethyl phosphonate, various placements of the proton being used for each of a series of spacings between the phosphoryl oxygen atom of the dimethyl phosphonate and the carboxylic oxygen atom of the formic acid. The O_2CH plane of the formic acid was placed in the plane of the H–P=O atoms of the dimethyl phosphonate and the following atoms lay on a line: $P{=}O \cdots H \cdots O{-}C$.

In the third case, the hydrogen directly bonded to the phosphorus of the dimethyl phosphonate was substituted by a fluorine atom; and the fourth case consisted of substituting a thiono-sulphur for the phosphoryl oxygen atom of the dimethyl phosphonate. The fifth case encompassed the model compound $(HO)_2(O\colon)P{\cdot}P(\colon S)(OH)_2$, where the OH groups were caused to be associated and proton(s) were brought up to the phosphoryl oxygen and/or the thiono-sulphur atom. The configuration chosen for this molecule places the O=P–P=S atoms in a plane with the added proton(s) also lying in this plane along the P=O and/or P=S axis. The angles and distances in all of these cases were selected from *X*-ray data on related molecules.[19, 20]

RESULTS AND DISCUSSION

Dialkyl Phosphonates $(RO)_2(H)PO$.—Previous investigators have found that dialkyl phosphonates undergo self-association ascribed[21] to ring formation involving a hydrogen atom directly bonded to the phosphorus of one phosphonate forming a hydrogen bond with the phosphoryl oxygen atom of another. Following the pattern of previous work,[22] we find that (even though the carboxylic acids are strongly self-associated[23]) a 1 : 1 azeotrope is formed between either dimethyl or diethyl phosphonate and acetic acid[24] or its monochloro-, dichloro-, or trichloro-derivatives.

When the isolated adducts were heated to 150 °C for several hours, decomposition by ester interchange led to formation of a two-phase system, the upper phase consisting primarily of the respective methyl or ethyl ester of the corresponding carboxylic acid and the lower phase esterified phosphorous acids (*e.g.*, 19% free acid, 55% monoester, and 26% diester in a sample studied by ^{31}P n.m.r. several months after the thermal treatment). The adducts of dimethyl phosphonate with either dichloro- or trichloro-acetic acid were observed to decompose by ester interchange when stored for one week at room temperature.

Analysis of both the ^{1}H and ^{31}P spectra[25,26] shows that the 1 : 1 adducts between the phosphonate and the various carboxylic acids exhibit a value of J_{PH} (for the coupling between the phosphorus and its directly bonded

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[14] K. Sasse, ' Houben–Weyl Methoden der Organischen Chemie,' 4th edn., Georg Thieme Verlag, Stuttgart, vol. 12/2, p. 294.

[15] See p. 85 of ref. 14.

[16] J. Michalski, W. J. Stec, and A. Zwierzak, *Bull. Acad. polon. Sci., Ser. Sci. chim.*, 1965, **13**, 677.

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[21] For example, see J. G. David and H. E. Hallam, *J. Chem. Soc.* (*A*), 1966, 1103 and references cited therein; also see R. Wolf, D. Houalla, and F. Mathis, *Spectrochim. Acta*, 1967, **23**, *A*, 1641.

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hydrogen) which is larger than J_{PH} for the pure phosphonate. This finding is in agreement with other studies [5,9] on the influence of hydrogen bonding.

Results from the ^1H and ^{31}P n.m.r. measurements on the adducts of dimethyl phosphonate with the various carboxylic acids studied are in Table 1, with similar data for dimethyl phosphonate in pure form, dissolved in carbon tetrachloride, and dissolved in several protonic solvents other than the carboxylic acids. These data show that not only does the coupling constant, J_{PH}, increase much in order of the ionization constant [27-29] of the solvent but there are also concomitant small downfield changes in the ^1H chemical shift, δ_H, of the hydrogen directly bonded to the phosphorus and, less consistently, in the ^{31}P chemical shift, δ_P. No correlation was observed with dielectric constant [30,31] or magnetic susceptibility [32] of the solvent.

TABLE 1

N.m.r. data on dimethyl phosphonate with protonic solvents

	Chemical shift			Coupling constant	
Solvent	δ_H[b]/p.p.m.	δ_P[c]/p.p.m.	δ_{OH}[d]/p.p.m.	$^1J_{PH}$/Hz	$\frac{J_{PH}}{(J_{PH})_{std}}$[e]
None	−6·7	−10·4		695·0	1·008
CCl_4 1 : 1[a]	−6·7	−10·3		693·1	1·006
1 : 2	−6·7	−9·9		692·6	1·005
1 : 5	−6·7	−9·4		691·9	1·004
1 : 10	−6·7	−9·2		691·9	1·004
$CHCl_2$ 1 : 1	−6·7	−10·7		697·2	1·012
1 : 2	−6·7	−10·6		697·6	1·012
1 : 5	−6·8	−10·5		697·2	1·012
1 : 10	−6·8	−10·5		697·5	1·012
MeOH 1 : 1	−6·8	−10·8		703[f]	1·020
1 : 2	−6·8	−11·5		705[f]	1·023
1 : 5	−6·8	−11·5		708[f]	1·027
1 : 10	−6·8	−11·4		709	1·029
PhOH 1 : 1	−6·6	−11·3		706·9	1·026
1 : 2	−6·5	−11·4		710·9	1·032
AcOH 1 : 1	−6·8	−11·2	−10·8	713·0	1·034
1 : 2	−6·8	−11·9	−11·1	715·0	1·038
1 : 5	−6·8	−11·9	−11·3	719·8	1·045
1 : 10	−6·8	−11·9	−11·4	719·9	1·045
$ClCH_2{\cdot}CO_2H$ 1 : 1	−6·9	−12·1	−11·8	713·2	1·035
1 : 2	−6·9	*f*	−11·6	716[f]	1·039
$Cl_2CH{\cdot}CO_2H$ 1 : 1	−6·9	−12·0	−12·6	723·1	1·049
1 : 2	−6·9	*f*	−11·9	729[f]	1·058
1 : 5	−7·0	*f*	−11·6	734[f]	1·065
1 : 10	−7·0	*f*	−11·6	734[f]	1·065
$Cl_3C{\cdot}CO_2H$ 1 : 1	−6·9	−11·6	−13·4	722·8	1·049
1 : 2	−7·0	−13·7	−12·2	727·6	1·056
$CF_3{\cdot}CO_2H$ 1 : 1	−6·8	−11·2	−13·8	714·4	1·037
1 : 2	−6·8	−12·1	−12·5	730·7	1·060
1 : 5	−6·9	−12·9	−11·9	734·1	1·065
1 : 10	−6·9	−13·0	−11·7	744·3	1·080
2N-H_2SO_4 1 : 1	−6·8	*f*		715[f]	1·037

[a] Mol ratio of solute to solvent. [b] Chemical shift of the phosphonate hydrogen atom, referenced to internal tetramethylsilane, with downfield shifts being negative. [c] Chemical shift of the phosphonate phosphorus atom, referenced to external 85% H_3PO_4, with downfield shifts being negative. [d] Chemical shift of the hydroxylic protons, measured as for *b*. [e] $(J_{PH})_{std}$ set equal to 689·0 Hz. This value was obtained from a 1 : 100 dilution with benzene. [f] Could not be measured accurately from the ^{31}P spectrum owing to decomposition or peak masking. Obtained from the ^1H spectrum at 60 MHz, if a value is given.

When an excess of the protonic solvent over the 1 : 1 mol ratio is employed, there is an additional increase in the value of J_{PH} for all of the protonic solvents, as shown in Table 1. This increase is in accord with the formation of more adduct, as would be expected from the effect of mass action on an equilibrium situation which is not strongly driven in one direction or the other. In the case of carbon tetrachloride (the only non-protonic solvent), increasing dilution of the dimethyl phosphonate leads to a decrease in the value of J_{PH}, in accord with a somewhat smaller coupling constant for the monomer than for the dimer. A value of $J_{PH} = 689{\cdot}0$ Hz was found for dimethyl phosphonate at a mol ratio of 1 : 100 in deuteriobenzene, by use of a deuterium lock. It was then assumed that $J_{PH} = 689{\cdot}0$ Hz represented infinite dilution in a non-reactive solvent, *i.e.* $(J_{PH})_{std}$ corresponds to monomeric molecules of the dimethyl phosphonate.

The general observations made for the dimethyl phosphonate were found, in a detailed study, to apply to

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[27] P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, 1960, **82**, 795.

[28] Handbook of Chemistry and Physics, 47th edn., Chemical Rubber Co., Cleveland, Ohio, 1966—67, D-86.

[29] J. L. Kurz and J. M. Farrar, *J. Amer. Chem. Soc.*, 1969, **91**, 6057.

[30] G. E. Maciel and G. C. Ruben, *J. Amer. Chem. Soc.*, 1963, **85**, 3903.

[31] See ref. 28, p. E-54.

[32] See ref. 28, p. E-108.

to the diethyl phosphonate. Dimethyl thiophosphonate, $(MeO)_2(H)PS$, was also investigated and it appears that in this case the effect of the protonic solvents leads to a maximum possible value of $J_{PH}/(J_{PH})_{std}$ of 1·013, where $(J_{PH})_{std}$ refers to the measurement at infinite dilution in a non-reactive solvent. This value is seen to be significant, but still relatively small compared with the data in Table 1 for the oxygen analogue. For $(MeO)_2(H)PS$ as a neat liquid, J_{PH} was found to be 652·2 Hz and the phosphorus chemical shift, δ_P, to be $-72{\cdot}7$ p.p.m.; whilst in a 1 : 2 solution in trifluoroacetic acid $J_{PH} = 659{\cdot}8$ and $\delta_P = -74{\cdot}3$ p.p.m.

Diethyl Phosphorofluoridate, $(EtO)_2(F)PO$.—Data from ^{19}F spectra show that $J_{PF}/(J_{PF})_{std}$ could probably not be larger than 1·009. For the neat liquid, $J_{FP} = 971{\cdot}1$ Hz, and $\delta_P = 8{\cdot}7$ p.p.m. upfield from 85% H_3PO_4, and $\delta_F = 82{\cdot}05$ p.p.m. upfield from $CFCl_3$. When this phosphorofluoridate was present in a 1 : 5 solution in trifluoroacetic acid, J_{PF} was 978·4 Hz, $\delta_P = +10{\cdot}5$, and $\delta_F = +84{\cdot}1$ p.p.m.

Since the change in coupling constant when going from one solvent to another is small in the case of the diethyl phosphorofluoridate, it could be argued that the observed effects are attributable primarily to dilution and are essentially wholly insensitive to hydrogen bonding of the protonic solvent molecules to the phosphoryl oxygen atom of the phosphorofluoridate. However, the change in the proton chemical shift of the hydroxy-group of trifluoroacetic acid is considerably greater upon dilution with diethyl phosphorofluoridate than with carbon tetrachloride. We therefore surmise that the observed changes from one protonic solvent to another are indeed attributable to hydrogen bonding, and that the association between the various acids and the phosphorofluoridate is weaker than the association between the same acids and the related phosphonate. The action of the fluorine substituent in diminishing the association between different phosphoryl compounds and phenol has been reported.[33]

Tetraethyl Monothiohypophosphate, $(EtO)_2(O\colon)P{\cdot}P({\cdot}S)(OEt)_2$.—This compound exhibits an unusually high phosphorus–phosphorus spin–spin coupling constant.[26] This led us to speculate that changes in J_{PP} upon increasing protonation would be readily measureable. Table 2 confirms that there is a significant increase in J_{PP} upon adding the more acidic solvents and this is accompanied by an upfield change in the ^{31}P chemical shift of the thiophosphoryl phosphorus atom and a downfield change in the chemical shift of the phosphoryl phosphorus atom.

TABLE 2

^{31}P N.m.r. data for tetraethylmonothiohypophosphate in protonic solvents

	Chemical shifts [b]		Coupling constant	
Solvent [a]	$\delta_{P(S)}$/p.p.m.	$\delta_{P(O)}$/p.p.m.	$^1J_{PP}$/Hz	$\frac{J_{PP}}{(J_{PP})_{std}}$ [b]
None	−73·3	−4·2	586·5	1·004
CCl_4 1 : 1	−73·0	−4·1	586·6	1·004
1 : 2	−73·0	−4·2	585·7	1·003
$CHCl_3$ 1 : 1	−72·9	−4·4	591·1	1·012
1 : 2	−72·8	−4·4	591·5	1·013
1 : 5	−72·7	−4·6	591·8	1·013
1 : 10	−72·7	−4·6	592·2	1·014
MeOH 1 : 1	−72·5	−4·2	595·9	1·020
1 : 2	−72·2	−4·2	597·2	1·023
1 : 5	−71·8	−4·2	600·8	1·029
PhOH 1 : 1	−71·9	−4·1	597·8	1·023
AcOH 1 : 1	−72·0	−4·1	598·3	1·024
1 : 2	−71·4	−4·1	603·5	1·033
$Cl_2CH{\cdot}CO_2H$ 1 : 1	−70·6	−4·2	607·9	1·041
1 : 2	*d*	−4·8	614·2	1·052
$CF_3{\cdot}CO_2H$ 1 : 1	−69·9	−4·1	612·2	1·048
1 : 2	−69·1	−4·5	614·8	1·053
1 : 5	−69·1	−4·9	618·8	1·059

[a] Mol ratio of solute to solvent. [b] Chemical shift from external 85% H_3PO_4 with downfield shifts being negative. [c] $(J_{PH})_{std}$ set equal to 584·0 Hz, by extrapolation. [d] Could not be obtained from the ^{31}P spectrum owing to decomposition of tetraethylmonothiohypophosphate.

The ^{31}P chemical shift of the impurity tetraethyl dithiohypophosphate $(EtO)_2(S\colon)P{\cdot}P(\colon S)(OEt)_2$ changes hardly at all from one solvent to another. This probably indicates that the hydrogen bonding preferentially involves the oxygen atom of the tetraethyl monothiohypophosphate to give the observed rather large changes in the phosphorus chemical shifts at both the thiophosphoryl and phosphoryl positions of the monothiohypophosphate.

As an additional example of the relatively large influence of protonic solvents on the phosphorus–phosphorus spin–spin coupling constants, data on 4,4,4′,4′-tetramethyl-1′-thioxo-1,1′-bi(phosphorinanyl)-1-one (I), have been obtained in dilute solutions (*ca.* 5%) in chloroform (J_{PP} 401 Hz) and in trifluoroacetic acid (J_{PP} 513 Hz).

Electronic Theory.—By utilizing the proper elements of the charge–bond-order matrix obtained from the

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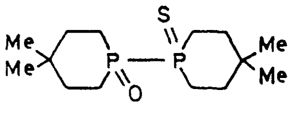
[33] G. Aksnes, *Acta Chem. Scand.*, 1960, **14**, 1475; G. Aksnes and T. Gramstad, *ibid.*, p. 1485; and G. Aksnes and P. Albriktsen, *ibid.*, 1968, **22**, 1866.

CNDO-SCF approximation [18] for an isolated rigid molecule, with *d*-character being allowed to the P and S



(I)

atoms, we have attempted to calculate (using the mean-excitation-energy approximation [34] with an invariant excitation energy) the subtle n.m.r. effects observed. In one group of studies, a proton was placed at various distances from the oxygen (or sulphur) atom along the P–O (or P–S) bond axis for the molecules $(MeO)_2P(H)O$, $(MeO)_2P(F)O$, and $(MeO)_2P(H)S$ to give the CNDO results shown in Figure 2. The total SCF energy calculated for the first two of these molecules was found to minimize at an O–H distance of *ca.* 0·96 Å and for the third at an S–H distance of *ca.* 1·34 Å. These distances are the same as those found in *X*-ray diffraction studies [20] for O–H and S–H bonds respectively so that the expected formation of a phosphonium ion from the interaction of the phosphonate and the proton is indeed predicted in the right bond length by the CNDO computation.

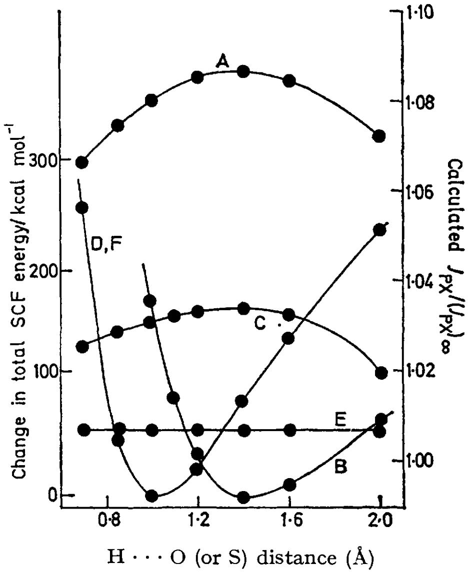


FIGURE 2 A plot showing the change in the total SCF energy (curves B, D, and F) and in the theoretically calculated $J_{HX}/(J_{HX})_\infty$ (curves A, C, and E) with X = H or F; A and B, $(MeO)_2(H)PS \cdots H^+$; C and D, $(MeO)_2(H)PO \cdots H^+$; E and F, $(MeO)_2(F)PO \cdots H^+$

As expected, association of the proton with the phosphoryl oxygen atom of the dimethyl phosphonate led to transfer of positive charge from the former to the latter and also further to the phosphorus. Appreciable charge transfer was also observed in more distant parts of the molecule as can be seen from the following calculated charge changes upon association of the proton at the position of minimum total energy: for the added proton, from +1·0 to +0·29; for the phosphoryl oxygen atom, from −0·38 to −0·22; for the phosphorus atom, from +0·50 to +0·65; for the hydrogen directly bonded to the phosphorus, from −0·07 to +0·04; and for each methoxy-oxygen atom, from −0·18 to −0·14. Analogous results were observed for the other molecules.

According to simple theory, [35] J_{PH} has been assumed to be proportional to the product [35] of (*a*) the diagonal term of the charge–bond-order matrix * representing the phosphorus 3*s* electrons, (*b*) the similar diagonal term for the directly bonded hydrogen 1*s* (or the fluorine 2*s*), and (*c*) the square of the off-diagonal cross term for this chosen pair of orbitals. The calculated values shown in Figure 2 for $J_{PX}/(J_{PX})_\infty$ where X stands for either H or F and the subscript ∞ refers to the unprotonated form, exhibit maxima for the $(MeO)_2(H)POH^+$ and $(MeO)_2(F)POH^+$ that are somewhat smaller than our respective experimental values. These results indicate that this simple theory, which cannot account [36] for the negative sign of the P–F coupling constant, gives a reasonable approximation for these cases probably because of the relatively small structural changes involved. We reason that the relatively large calculated value of $J_{PP}/(J_{PP})_\infty$ for $(MeO)_2(H)PSH^+$ may indicate a rather large increase in the P–H coupling constant owing to proton–sulphur association along with a lesser equilibrium constant for such association (as compared with proton–oxygen association) so that the ratio of the experimental to the calculated value of $J_{PH}/(J_{PH})_\infty$ would be smaller than unity, as observed.

For the hypophosphate model compound, $(HO)_2(O\!:\!)P{-}P(\!:\!S)(OH)_2$, the maximum calculated value of $J_{PP}/(J_{PP})_\infty$ was 1·145 when one proton was brought up to the oxygen and another to the sulphur atom. This large value is commensurate with the relatively large experimental value for tetraethyl monothiohypophosphate. Surprisingly, $J_{PP}/(J_{PP})_\infty$ remained essentially unity when a single proton was brought up to the oxygen atom alone; and $J_{PP}/(J_{PP})_\infty$ exhibited a maximum value of 1·06 when a single proton was brought up to the sulphur atom.

The CNDO study of formic acid and dimethyl phosphonate showed that for the most stable situation the shared proton was closer (1·10 Å) to the oxygen atom of the formic acid than it was to the phosphonate oxygen atom (1·30 Å). The charge on this proton was calculated to be +0·236. The theoretical value of $J_{PH}/(J_{PH})_\infty$ was 1·001.

An attempt to interpret the chemical-shift changes by use of the appropriate terms (involving only *p* and *d*

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* Note that theory employs the appropriate orbital changes evaluated at the nuclei for each of the coupled nuclei. However, when a single fixed orbital exponent is used for each atomic orbital, this charge is directly proportional to the pertinent diagonal term of the charge–bond-order matrix.

[34] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 460.

[35] See equation (1) in P. D. Ellis and G. E. Maciel, *J. Amer. Chem. Soc.*, 1970, **92**, 5829.

[36] W. McFarlane, *Quart. Rev.*, 1969, **2**, 187.

orbitals) from the charge and bond-order matrix[37] and assuming no change in mean excitation energy upon protonation was disappointing in that some of the theoretically calculated shift changes were in the opposite direction from the experimental observations and the absolute magnitudes of these changes did not increase in the same order from molecule to molecule as was experimentally observed. The calculated shift changes were reasonable and in the right direction for the ^{31}P results on $(MeO)_2P(F)O$ and for the phosphorus bonded to the thiono-sulphur in the analogue of tetraethyl monothiohypophosphate.

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[37] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1964, **40**, 1714 [see equation (5), using an invariant Δ and $\langle 1/r^3\rangle_p$ and setting $\langle 1/r^3\rangle_d/\langle 1/r^3\rangle_p = 0{\cdot}010$ from spectrographically determined spin–orbit coupling constants].