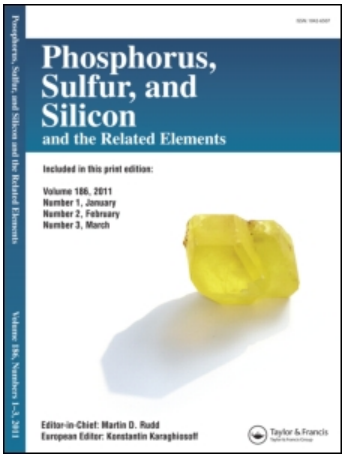

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A NOVEL SUBSTITUENT EFFECT ON ^{31}P NMR CHEMICAL SHIFTS IN THE ARYL DIPHENYLPHOSPHINATE SERIES

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A NOVEL SUBSTITUENT EFFECT ON ^{31}P NMR CHEMICAL SHIFTS IN THE ARYL DIPHENYLPHOSPHINATE SERIES

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The ^{31}P NMR chemical shifts of a series of meta- and para-substituted phenyl diphenylphosphinates, $Ph_2P(O)OC_6H_4$–X, have been determined. The δ ^{31}P values exhibit an increasing downfield trend as the electron-withdrawing properties of the substituent X become greater and a reasonable correlation between δ ^{31}P and Hammett–Taft substituent constants is obtained. This trend is opposite to that exhibited in several families of compounds of the type $ArP(O)Y_2$, where δ ^{31}P values show an increasing upfield trend as the electron-withdrawing ability of the substituent in Ar is increased. The results are explained by proposing varying degrees of d-orbital occupancy in the phosphorus–oxygen bonds (P–OAr and P=O) in the series of compounds as a factor influencing ^{31}P chemical shifts.

INTRODUCTION

Structural and electronic effects on phosphorus-31 NMR chemical shifts continue to be of considerable interest as the application of ^{31}P NMR to problems of chemical and biochemical importance increases.[1] A number of attempts to develop a unified theoretical foundation for ^{31}P chemical shifts have been made, and factors such as electronegativity differences, π-electron overlap and σ-bond angles between phosphorus and the atoms or groups bonded to it have been identified as contributing to the origin of the chemical shifts.[2] However, in order to separate these factors it has been found useful to limit the number of variables and to determine ^{31}P chemical shifts within a class of structurally related compounds, as for example through substituent changes on a phenyl moiety attached to phosphorus. This approach could give information on polar and resonance effects, by examining the relationship between ^{31}P chemical shifts and Hammett-Taft substituent parameters.

The interesting observation was made in studies of the series of compounds **1–4** containing different X substituents on the meta and para positions of the phenyl moiety, that electron-withdrawing substituents lead to an upfield shift of the ^{31}P signal, pointing to a shielding effect on the phosphorus atom.[3–6] The opposite behaviour is found normally, as for example in families of benzenoid compounds of the type $ArCH_2Y$, when the ^{13}C or ^{1}H chemical shifts of the CH_2Y group are

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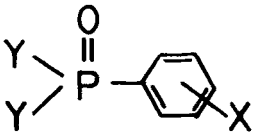
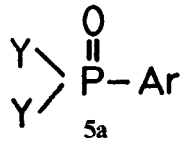
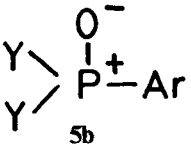


1 - 4 (Y = F, Cl, OH, OEt)

examined as a function of substituent changes in the aryl moiety. The suggested explanation for the shielding effect in the series **1**–**4** invoked increased P=O $d\pi$–$p\pi$ bond order as a result of greater contribution by the resonance structure **5a** relative to **5b**, due to an electron-withdrawing substituent in the aryl group.[7] However, some difficulties associated with this explanation have been pointed out.[2]

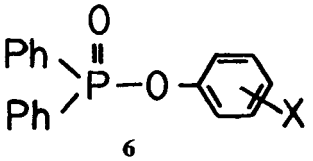


5a



5b

In the present work we have determined the ^{31}P chemical shifts of the series of aryl diphenylphosphinates **6**, in which substituent changes are introduced on the benzene ring separated from the phosphorus by an oxygen atom. In contrast to the foregoing studies,[3-6] we have found a normal relationship between ^{31}P chemical shifts and the electron-withdrawing properties of X; that is, a downfield trend in δ ^{31}P with increased electron-withdrawing ability of the substituent.



6

RESULTS AND DISCUSSION

A series of ten substituted diphenylphosphinates (**6**) was prepared, as part of a kinetic study,[8] by the reaction of chlorodiphenylphosphine oxide with the appropriate substituted phenol in the presence of triethylamine. The ^{31}P NMR spectra were determined in $CDCl_3$ solution with 85% phosphoric acid as an external standard. The chemical shifts of the individual compounds are given in Table I.

The ^{31}P chemical shifts of compounds **6** correlate reasonably well with the Hammett σ parameters of the substituents on the phenoxy moiety. This linear relationship can be described by the following equation:

$$\delta\ ^{31}P = 2.43\sigma + 31.13 \qquad (r = 0.954) \tag{1}$$

Replacing σ by the Hammett–Taft σ^0 constants (which were preferred in another study[3]) gives a slightly better correlation (Eq. 2) as shown in Figure 1,

$$\delta\ ^{31}P = 2.26\sigma^0 + 30.97 \qquad (r = 0.975) \tag{2}$$

TABLE I

^{31}P Chemical shifts and physical constants of substituted phenyl diphenylphosphinates

$Ph_2P(O)OC_6H_4$–X X	m.p. °C (lit. value)	σ	σ^0	δ ^{31}P (ppm)[a]
p-MeO	96 (96–98)[13]	−0.27	−0.16	30.80
p-Me	121–122 (119.5–121)[13]	−0.17	−0.12	30.52
H	137–138 (136–138)[13]	0	0	30.85
p—F	107	0.06	0.17	31.53
p-Br	111 (118)[14]	0.23	0.26	31.74
p-CH_3CO	115 (113–115)[13]	0.50	0.46	31.87
p-CF_3	106–107	0.55	0.53	32.17
p-CN	90–91	0.66	0.69	32.89
m-NO_2	126 (124)[13]	0.71	0.70	33.23
p-NO_2	151 (149)[12] (156)[13]	0.78	0.82	33.10

[a] In $CDCl_3$ with 85% H_3PO_4 as external standard.

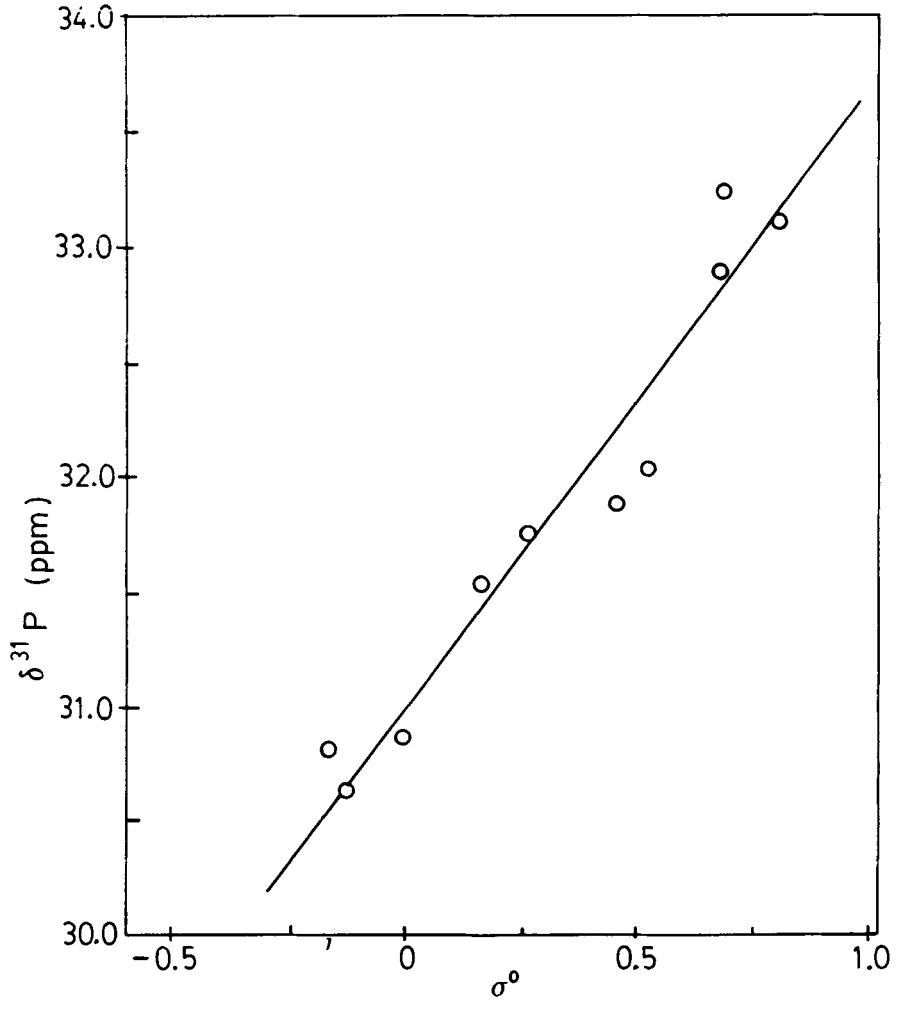
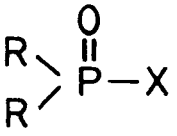


FIGURE 1 Plot of ^{31}P chemical shifts of the substituted phenyl diphenylphosphinates (Table I) versus Hammett–Taft σ^0 parameters.

though it is not clear whether this somewhat better correlation is indeed of any fundamental significance.

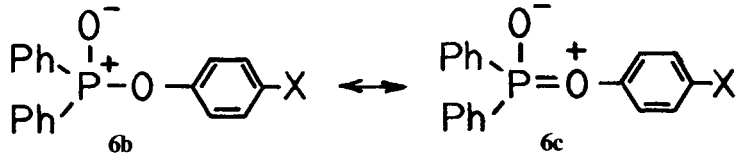
The most important outcome of the present work is the trend observed in the chemical shifts. The experimental results clearly indicate that an increase in the electron-withdrawing power of the substituent is accompanied by a downfield shift of the ^{31}P resonance. This appears to be the first instance of a "normal" relationship between the ^{31}P chemical shift and the effect of substituents on a phenyl group. However, a previous case in which "normal" behavior was observed involved a moiety directly bonded to the phosphorus atom. Thus Schmidpeter and Brecht[9] found that ^{31}P chemical shifts of several phosphinyl derivatives (**7**) correlated linearly with the Hammett substituent constants and that the shielding increased on increasing the efficiency of the moiety X as an electron donor (e.g. X = Cl, OCH_3, $N(CH_3)_2$, O^-).



7 (R = Me, Ph)

It was stated earlier that the state of d-orbital occupancy is apparently one factor influencing ^{31}P chemical shifts.[7] Thus, placing an electron-withdrawing group on a phenyl ring directly attached to the phosphorus atom would deplete the net charge on the phosphorus, which in turn would enhance phosphoryl $d\pi$–$p\pi$ bonding. Hence increasing the extent of d-orbital occupancy apparently induces an upfield shift in the ^{31}P resonance which outweighs the downfield shift normally expected on decreasing the electron density around the phosphorus atom.

In the series of compounds examined here, a different kind of bonding situation may exist. It is now possible to propose a contribution by resonance structure **6c** which would result from donation of an electron pair in a p-orbital on the phenoxy oxygen to a d-orbital of the partially positive phosphorus atom as shown in **6b**:

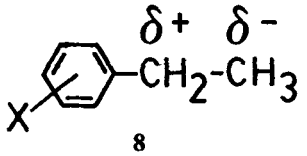


6b **6c**

The contribution by **6c** would be enhanced by electron-donating substituents X and since this would lead to increased d-orbital occupancy, a shielding effect on the ^{31}P chemical shift would result. Conversely, electron-withdrawing substituents, through decreasing the contribution of **6c**, would cause decreased d-orbital occupancy and hence lead to deshielding.

The explanation proposed for the present results is thus similar in kind to that used in the foregoing explanation of "abnormal" ^{31}P chemical shifts in that, in both types of systems, changes in d-orbital occupancy induced by the substituents on the phenyl ring are proposed as the causes of the chemical-shift changes.

A different kind of explanation for the changes in the ^{31}P chemical shifts can be considered, by drawing analogy between the phosphorus compounds **1–4** and **6**, and the ethylbenzene system **8**.



8

In the latter case the substituents on the ring affect the chemical shifts of the α and β carbon atoms in opposite ways. The chemical shift of the ^{13}C atom at the α position moves downfield as the substituent X becomes more electron withdrawing, whereas that of the β carbon moves upfield.[10] This behaviour was traced to the charge-alternation principle advanced by Pople *et al.*[11] The phosphorus atom in the families **1–4** and **6** would also respond to substituent change according to its position relative to the phenyl ring. When located at the α position (i.e. **1–4**), an increase in the electron-withdrawing ability of its substituent would induce an upfield shift, whereas at the β position (i.e. **6**) its chemical shift would move downfield. However, although in both the carbon and the phosphorus compounds the substituent effects are reversed in the α and the β positions, the trend in the phosphorus system is opposite to that in the carbon analogue. Therefore, it appears unlikely that the charge-alternation effect is the determining factor in governing the chemical shift of the phosphorus atom in this family of compounds.

EXPERIMENTAL

The phosphinates used in this study were prepared by the following general method (see also refs. 12–14). Chlorodiphenyl phosphine (100 g) was oxidised and hydrolysed to diphenylphosphinic acid by slow addition, with stirring, to 100 ml of 30% hydrogen peroxide. An oily mass is produced initially but after addition of 50 ml of ethanol and stirring for ca. 3 h white crystals are formed. Recrystallization from ethanol yielded a solid, m.p. 199°. The phosphinic acid (0.01 mole, 2.18 g) was converted to chlorodiphenylphosphine oxide by addition of 10 ml of thionyl chloride. At completion of the reaction the excess thionyl chloride was distilled off, leaving the chlorodiphenylphosphine oxide residue. To a solution of the latter in 100 ml anhydrous ether was added slowly with stirring a solution of the particular phenol (0.011 mole) and triethylamine (5 ml) in ether (100 ml) and the reaction mixture was stirred for 24 h. The precipitate of the amine hydrochloride which formed was collected by filtration, washed with ether and the combined filtrate and washings were evaporated to dryness. The product was recrystallised from acetone-petroleum ether. The characteristics of the compounds prepared are given in Table I.

The ^{31}P NMR spectra were obtained in $CDCl_3$ solutions on a Bruker CXP 200 MHz instrument operating at 80.982 MHz, with 85% H_3PO_4 as external standard.

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