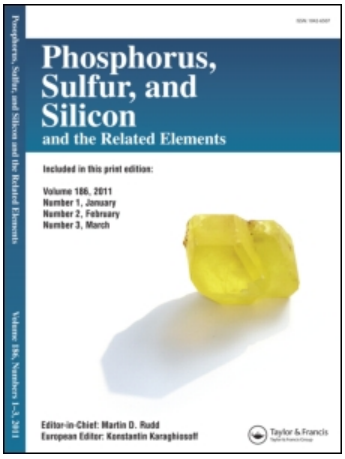

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ELECTRONIC STRUCTURE AND ^{31}P NMR CHEMICAL SHIFT OF SUBSTITUTED TRIARYL, DIARYL METHYL AND DIMETHYL ARYL PHOSPHATES-A SEMI-EMPIRICAL MOLECULAR ORBITAL APPROACH

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ELECTRONIC STRUCTURE AND ^{31}P NMR CHEMICAL SHIFT OF SUBSTITUTED TRIARYL, DIARYL METHYL AND DIMETHYL ARYL PHOSPHATES—A SEMI-EMPIRICAL MOLECULAR ORBITAL APPROACH

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The ^{31}P NMR chemical shift of triaryl phosphate, diaryl methyl phosphate and dimethyl aryl phosphate series was determined. The δ^{31}P values exhibit an increasing downfield trend when aryl substituents are exchanged for alkyl groups and δ^{31}P values show an increasing upfield trend as the electron-withdrawing ability of the substituent in the aromatic ring is increased. Semi-empirical calculations showed an increasing positive charge on phosphorus atom and an increasing phosphoryl bond order when δ^{31}P values go upfield. These results are in agreement with the effect of "back bonding" from the phosphoryl oxygen to the phosphorus atom.

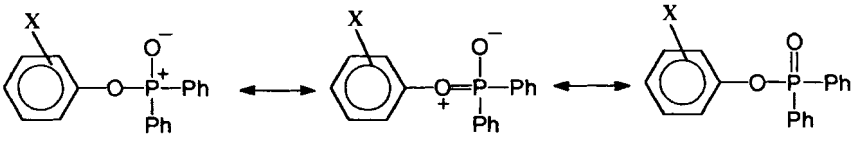
Keywords: ^{31}P NMR chemical shifts; structural effects; molecular orbitals; triaryl phosphates; diaryl alkyl phosphates; dialkyl aryl phosphates

INTRODUCTION

The effect of substituents at the phenyl ring of aromatic organophosphorus compounds, on ^{31}P NMR chemical shift, is reported in the literature. Electron withdrawing groups located in the substituted phenoxy ring of aryl phosphinates (**1**) led to a deshielding effect on the phosphorus atom while electron donating groups led to a shielding effect.[1,2] This was attributed to an enhanced d-orbital occupancy that would be better represented by resonance structure (**1b**).[1]

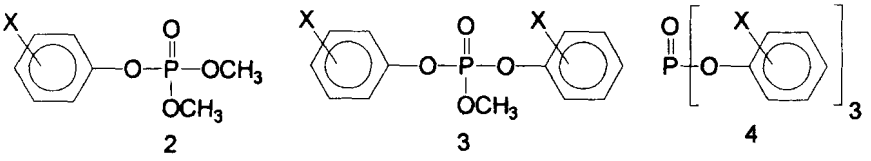
Li and coworkers observed that the above explanation was inconsistent with similar phosphonic and phosphoric acid derivatives, since it showed an opposite trend for these functions. The effect of substituents on the ^{31}P NMR chemical shift of dihexyl aryl phosphates, for example, showed that electron withdrawing substituents led to a shielding effect on the phosphorus atom and electron donating groups led to a deshielding effect. It has been proposed, for tetracoordinate phosphorus compounds, that the ^{31}P NMR chemical shift is mainly governed by symmetry of the electron cloud on the phosphorus atom that would in turn be related to the electronegativity of the substituents.[3]

Another suggested explanation for the above behavior invoked an increased phosphoryl $d\pi$-$p\pi$ bond order as a result of greater contribution of a similar resonance structure for phosphinates (**1c**),[4] that would be increased by electron withdrawing substituents.



A molecular orbital approach to this problem was thought to give a better picture of the electronic structure of these compounds and a better basis for discussing the above speculations. Semi-empirical calculation has been used as a suitable method for calculating electron structure of complex organic molecules because, in their areas of applicability, results are comparable with those obtained from "ab initio" methods, at less than one-thousandth of the cost in computing time.[5] Parameters for AM1 Hamiltonian[6] were developed to give satisfactory results for both trivalent and pentavalent phosphorus not considering the *d* atomic orbitals.[7]

The aim of this paper is to define the effect of electron withdrawing and electron donating substituents on the ^{31}P NMR chemical shift of dimethyl aryl phosphates (**2**), diaryl methyl phosphates (**3**) and triaryl phosphates (**4**). Semi-empirical calculations (AM1 Hamiltonian) were used to calculate charge densities on the phosphorus atom, the bond order of the phosphoryl unit and the π electron contribution to the phosphoryl bond order. It is expected that the omission of *d* orbitals in this treatment would not impair significantly the directions of the expected results, since a Mulliken[8] breakdown of one such oxygen lone pair showed, from "ab initio" calculations for the hypothetical molecule H_3PO, convincing evidence that the π back donation in these lone pairs is primarily toward *p* rather than to *d* orbitals.[9]



2 3 4

RESULTS AND DISCUSSION

Triaryl phosphates were synthesized by reacting phosphoryl chloride with the appropriate substituted sodium phenoxide.[10,11] Diaryl methyl and dimethyl aryl phosphates were obtained by transesterification of the appropriate substituted triaryl phosphate with sodium methoxide.[10,12] All compounds were purified by flash chromatography[13] using hexane/ethylacetate (30%) as eluent and the characterization of the products was achieved using FTIR, GC-MS, ^{1}H NMR and ^{31}P NMR (TABLE I).

It can be seen from TABLE I that an increase in the electron withdrawing power of the substituents on the phenyl ring led to a shielding effect on the phosphorus atom in all three classes of phosphates.

The semiempirical calculations showed an increase in positive charge on phosphorus (Qp) when alkyl substituents were exchanged for aryl groups. The same profile was observed when the electron withdrawing power of substituents on aromatic ring increased (FIGURE I).

These calculations also showed, in relation to the same structural changes, a rise in the phosphoryl bond order (BO) (FIGURE II) and in the related π contribution (πc) (FIGURE III), which could have been induced by the positive charge enhancement on phosphorus atom (FIGURE IV). This behavior indicates a possible "back-bonding" effect that is also in accordance with the decrease in the phosphoryl oxygen negative charge (Qo) (FIGURE V).

The calculated linear correlation for the above relationship leads to the following equations (a–e) and R^2 values.

$$\delta^{31}P = -0.0035\ Qp + 2.554 \quad (R^2 = 0.9343) \qquad (a)$$

$$\delta^{31}P = -0.0023\ BO + 1.173 \quad (R^2 = 0.8965) \qquad (b)$$

$$\delta^{31}P = -0.0022\ \pi_c + 0.318 \quad (R^2 = 0.9401) \qquad (c)$$

TABLE I Spectrometric data of compounds

No.	*X*	*^1H NMR[a] Multiplicity and relative peak area*	*^{31}P NMR[b] signal multiplicity*	*J_{P-H} (Hz)*	*IR (cm^{-1}) P=O*	*IR (cm^{-1}) P-O-C*	*MS (m/z) M^+*	*MS (m/z) base peak*
2a	H	3.8 (6H,d); 7.3 (5H,m)	−6.4 (m)	11.3	1288	1192, 1164, 1041	202	90
2b	4-Cl	3.9 (3H,d); 7.(1H,m); 7.4 (1H,m)	−6.5(hep)	11.3	1292	1223, 1046, 952	236	109
2c	2,4-Cl	3.8 (3H,d); 3.9 (3H,d); 7.3 (1H,m); 7.4(2H,m)	−6.9(m)	11.4	1292, 1261	1237, 1101, 1050, 956	270	235
3a	4-Cl	4.0 (3H,d); 7.2 (4H,m); 7.3 (4H,m)	−13.4(q)	11.6	1299	1196, 1051, 958	332	127
3b	2,4-Cl	4.1 (3H,d); 7.2 (2H,m); 7.3 (2H,m); 7.4 (2H,m)	−14.2(q)	11.9	1305, 1257	1223, 1102, 1065, 940	402	133
3c	4-NO_2	4.1 (3H,d); 7.5 (4H,m); 8.3 (4H,m)	−14.8(q)	11.8	1299	1199, 1053, 951	–	–
4a	H	7.3 (1H,m)	−19.9(s)	–	1303	1190, 950	326	326
4b	CH_3	2.3 (3H,s); 7.1 (4H,m)	−19.1(s)	–	1304	1186, 1140, 962	368	368
4c	4-Cl	7.2 (1H,m); 7.3 (1H,m)	−20.1(s)	–	1301	1197, 1092, 984	428	77
4d	2,4-Cl	7.3 (1H,m); 7.4 (2H,m)	−21.1(s)	–	1308	1222, 1149, 1014, 978	–	–
4e	4-NO_2	7.5 (1H,d); 8.3 (1H,d)	−22.2(s)	–	1308	1191, 1160, 959	–	–

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

$$Q_P = 1.3\ BO + 0.991 \quad (R^2 = 0.8677) \tag{d}$$

$$\delta^{31}P = -0.0013\ Qo - 1.081 \quad (R^2 = 0.7757) \tag{e}$$

The same kind of calculation has been done for the aryl oxygen-phosphorus bond but the linear correlation coefficient (R^2) was about 0.2655. It is evident that the aryl oxygen does not contribute substantially to the shielding effect observed on phosphorus atom. These results are in agreement with Li's statement,[2] but their model of "electron cloud symmetry" showed a poorer linear correlation when applied to our series (R^2 = 0.0256).

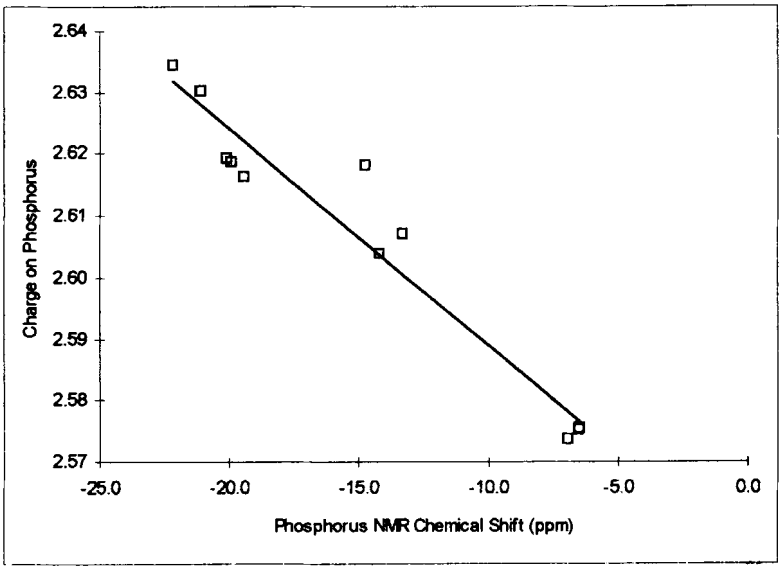


FIGURE 1 Relationship between the charge on phosphorus (Qp) and the ^{31}P NMR chemical shift for substituted triaryl, diaryl methyl and dimethyl aryl phosphates.

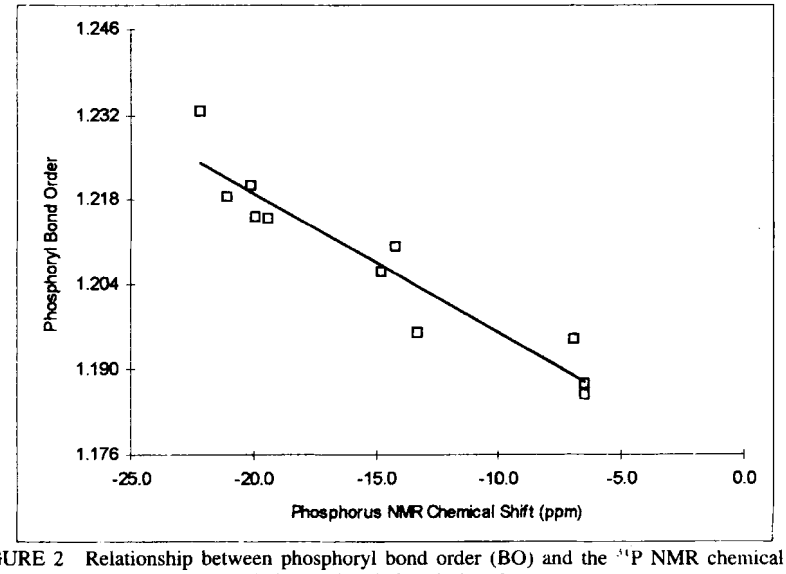


FIGURE 2 Relationship between phosphoryl bond order (BO) and the ^{31}P NMR chemical shift for substituted triaryl, diaryl methyl and dimethyl aryl phosphates.

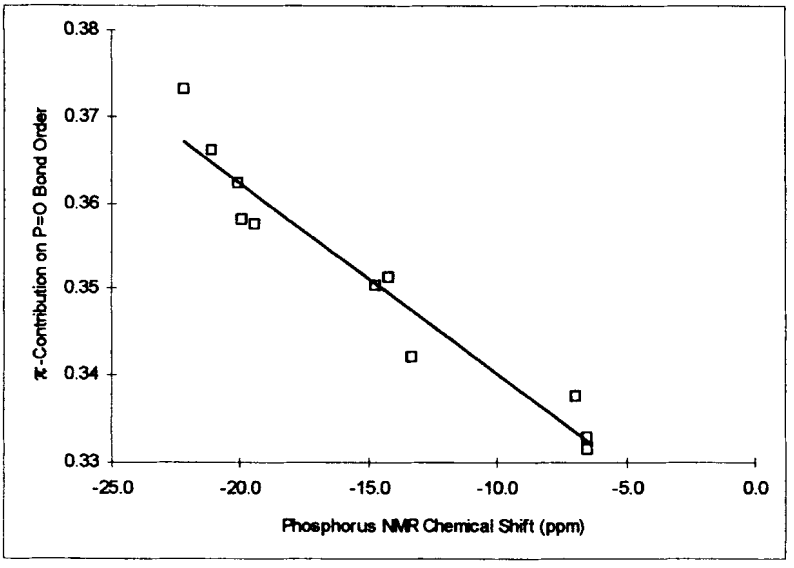


FIGURE 3 Relationship of the π contribution to phosphoryl bond order (π_c) and the ^{31}P NMR chemical shift for substituted triaryl, diaryl methyl and dimethyl aryl phosphates.

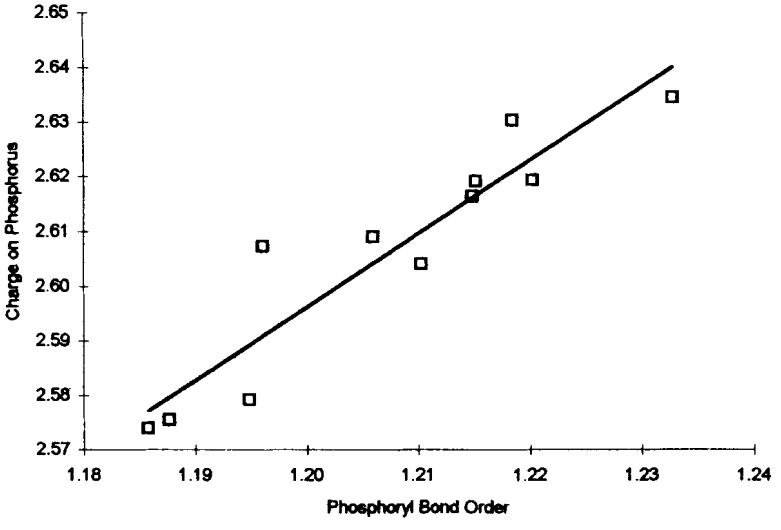


FIGURE 4 Relationship between charge on phosphorus and the phosphoryl bond order (BO) for substituted triaryl, diaryl methyl and dimethyl aryl phosphates.

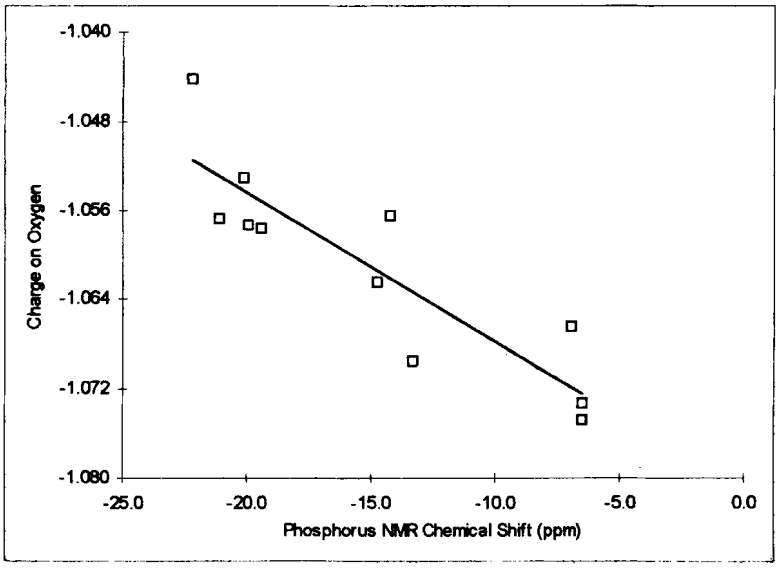
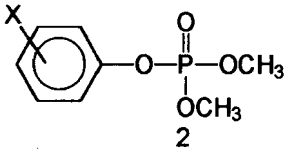


FIGURE 5 Relationship between the charge on phosphoryl oxygen (Qo) and the ^{31}P NMR chemical shift for substituted triaryl, diaryl methyl and dimethyl aryl phosphates.

The analysis of the above results suggests that the structures 2a, 3a and 4a are better pictures of the electronic state around the phosphorus atom but the importance of 2, 3 and 4 increases as the electron withdrawing power of the groups present in the aromatic ring intensifies.



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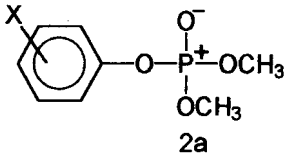
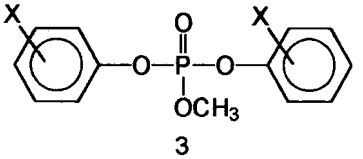


2a



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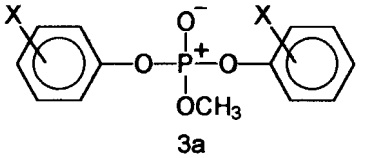
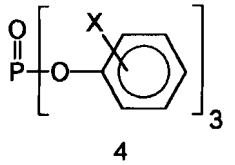


3a



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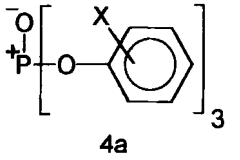

4a

EXPERIMENTAL

Infrared spectra were recorded on a Nicolet 740 FTIR spectrophotometer. ^{1}H NMR (200 MHz) and ^{31}P NMR (81 MHz) spectra were recorded on a Bruker HC200. $CDCl_3$ was used as solvent and chemical shifts were expressed in δ (ppm) units using TMS as internal reference for ^{1}H spectra and H_3PO_4 as external reference for ^{31}P. Electron impact mass spectra were recorded on a Hewlett-Packard 5790 at 70 eV.

The most stable conformation of the simplest phosphate of each series (for example, triphenyl phosphate in the triaryl phosphates series) was obtained using the INSIGHT II/DISCOVER-BIOSYM VERSIONS 2.1.0 and 2.8.0 softwares respectively with the Consistent Valence Forcefield (CVFF)[14] and Newton-Raphson minimization algorithms. To achieve the most stable conformation, each bond (except P—O phosphoryl bond) was rotated through a complete revolution in 20-degree increments, with the minimization of energy to each bond. Assuming that the substituent on the aromatic ring would not substantially affect the respective conformation map, one hydrogen atom of the aromatic ring was replaced with the appropriate substituent and a next minimization was performed. Charge densities and bond orders were obtained from the semi-empirical optimized structures using MOPAC 6.0 version with the AM1 Hamiltonian.

General Method for the Synthesis of Triaryl Phosphates

tris(p-nitrophenyl) phosphate (4e)

To a mechanically stirred suspension of 112 g of dried and finely powdered sodium p-nitrophenoxide in 400 ml of methylene chloride, 16 mL of phosphorus oxychloride were added dropwise at room temperature and the reaction medium refluxed for 2 hours. The reaction medium was cooled gradually to $-10°C$. The mixture of solids which separated was filtered and repeatedly washed with cold water until the washings were colorless. The crystalline residue was recrystallized from ethyl acetate. The yield was around 90% for all triaromatic phosphates prepared (see also ref.[10]).

General Method for the Synthesis of Diaryl Methyl Phosphates and Aryl Dimethyl Phosphates

bis (p-nitrophenyl)methyl phosphate (3c)

To a stirred solution of 4.61 g (0.01 mol) of tris-p-nitrophenyl phosphate (**4e**) in 300 mL of methylene chloride at room temperature, a methanolic solution of sodium methoxide [0.23 g (0.01 mol) of sodium per 300 mL of methanol] was

added dropwise. The reaction mixture was stirred for another 30 minutes and the precipitated sodium p-nitrophenoxide filtered off. The filtrate was extracted with water until the washings were colorless. The solvent was removed under vacuum. The product was purified by "flash chromatography"[13] using a mixture of hexane/ethyl acetate 30% as eluent. The yield for the different products was between 75 and 93% (see also ref.[10]).

The aryl dimethyl phosphates were prepared using the same procedure only doubling the amount of sodium methoxide.

Acknowledgements

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