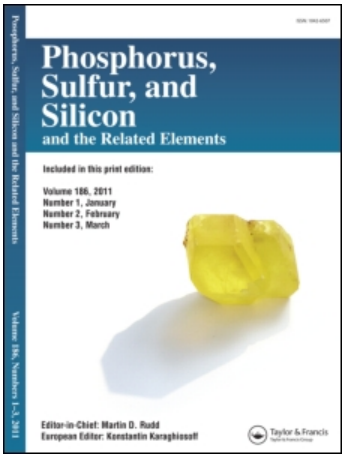


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

AB-INITIO CALCULATIONS OF ^{31}P NMR CHEMICAL SHIFTS OF SUBSTITUTED ARYL DIALKYL PHOSPHATES

Marcelo S. Pedrosa[abc]; João F. Cajaiba Da Silva[a]
[a] Universidade Federal do Rio de Janeiro, Instituto de Química, Pólo de Xistoquímica, Rio de Janeiro, Brasil [b] Universidade do Grande Rio, ICEN, [c] ETFQ-UNED-Nilópolis-RJ,

To cite this Article Pedrosa, Marcelo S. and Silva, João F. Cajaiba Da(2001) 'AB-INITIO CALCULATIONS OF ^{31}P NMR CHEMICAL SHIFTS OF SUBSTITUTED ARYL DIALKYL PHOSPHATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 170: 1, 233 — 246
To link to this Article: DOI: 10.1080/10426500108040601
URL: http://dx.doi.org/10.1080/10426500108040601

Phosphorus, Sulfur and Silicon, 2001, Vol. 170, pp. 233-246
Reprints available directly from the publisher
Photocopying permitted by license only

AB-INITIO CALCULATIONS OF ^{31}P NMR CHEMICAL SHIFTS OF SUBSTITUTED ARYL DIALKYL PHOSPHATES

MARCELO S. PEDROSA[abc*] and JOÃO F. CAJAIBA DA SILVA[a†]

[a]Universidade Federal do Rio de Janeiro, Instituto de Química, Pólo de Xistoquímica, Cidade Universitária, Rio de Janeiro, Brasil, 21494-900, [b]Universidade do Grande Rio, ICEN and [c]ETFQ-UNED-Nilópolis-RJ

(Received August 07, 2000; In final form November 12, 2000)

The experimental values of ^{31}P NMR chemical shifts of dialkyl aryl phosphates were compared to the ab-inito calculated values. The consistence of the model that states the δ^{31}P NMR chemical shift of phosphoric acid derivatives is mainly governed by symmetry of the electron cloud on the phosphorus atom that would, in turn, be related to the electronegativity of the substituent and the model suggesting the effect of "back bonding" from phosphoryl oxygen to phosphorus atom were both confirmed.

Keywords: ^{31}P NMR; structural effects; substituted aryl dialkyl phosphates; molecular orbital; ab-initio

INTRODUCTION

The effect of substituents on the phenyl ring of aromatic organic phosphorus compounds on ^{31}P NMR chemical shift is strongly related to the phosphorylated function type. In simple and phenyl-substituted saturated ciclic phosphines, a shielding effect was observed on the phosphorus atom in terms of the HOMO/LUMO energy gap and the increased p-character of the phosphorus lone pair[1,2]. Electron withdrawing groups located in the aromatic rings of phosphinates led to a deshielding effect on the phosphorus atom while electron donating groups led to a shielding effect. This was attributed to an enhanced d-orbital occupancy[3]. The phosphonic and phos-

* phone 55 21 5900990, fax: 55 21 5904472.
† e-mail: caj@iq.ufrj.br

phoric acid derivatives showed a trend in the opposite direction[4]. For this situation, it has been proposed, for tetracoordinate phosphorus compounds, that the ^{31}P NMR chemical shift is mainly governed by the symmetry of the electron cloud on the phosphorus atom that would, in turn, be related to the electronegativity of the substituent [4]. In aromatic phosphates, this behavior was attributed to an enhanced d-orbital occupancy. Semi-empirical calculations showed an increasing positive charge on the phosphorus atom and an increasing phosphoryl bond order as $\delta^{31}P$ values go upfield. These results are in agreement with the effect of "back bonding" from phosphoryl oxygen to phosphorus atom[5].

Organic phosphates have been used as nucleotide analogs with activity against some virus and bacteria[6,7] and as prodrugs for several deseases[8]. Owing these facts, further knowledge of the electronic state around the phosphorus atom in phosphates becomes a very important study matter.

The aim of this work was to perform ab-initio calculation of ^{31}P NMR chemical shifts and to determine some geometric and electronic parameters for substituted dialkyl aryl phosphates in order to aid the checking of the models cited above.

RESULTS AND DISCUSSION

The ^{31}P NMR chemical shifts for various structures were calculated and compared with the values cited in the literature as can be soon in TABLE I and FIGURE 1.

TABLE I Experimental and calculated ^{31}P NMR chemical shifts for dihexyl aryl phosphates

Compounds	$\delta^{31}P$ *lit*[4]	$\delta^{31}P$ *calc.*
Dihexyl-p-methoxy-phenyl phosphate	−7.40	−7.16
Dihexyl-p-methylphenyl phosphate	−7.61	−7.66
Dihexyl-phenyl phosphate	−7.86	−7.86
Dihexyl-p-chlorophenyl phosphate	−7.97	−7.87
Dihexyl-p-bromophenyl phosphate	−8.30	−7.93
Dihexyl-p-nitrophenyl phosphate	−8.81	−8.48

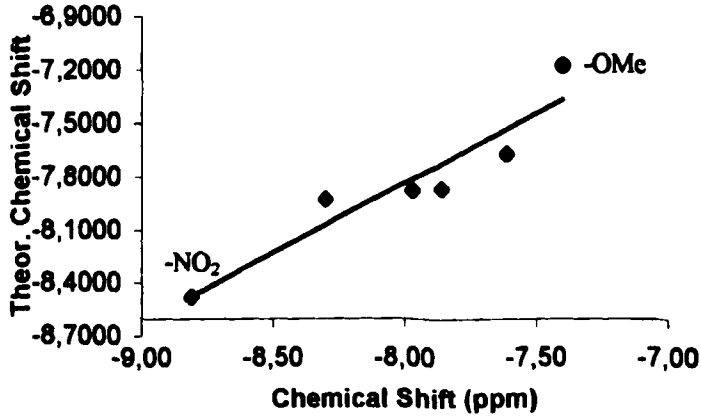
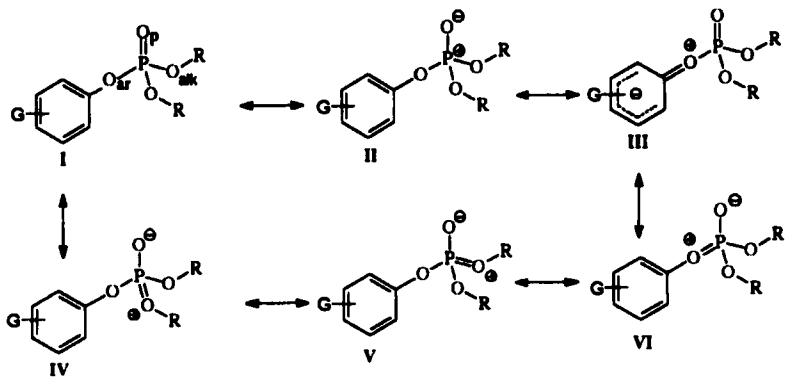


FIGURE 1 Relationship between the calculated and experimental ^{31}P NMR chemical shift for aryl dihexyl phosphates (R^2=0.883 and slope=0.790). R^2=0.879 and slope=0.605 for aryl diethyl phosphates. R^2=0.887 and slope=0.793 for aryl dibutyl phosphates

The resonance structures showed in SCHEME 1 summarize the main results obtained.



SCHEME 1 Substituted aryl dialkyl phosphate's canonical resonance structures R= Ethyl, butyl or hexyl and G=p-OMe, p-Me, H, p-Cl, p-Br or p-NO_2

The electron withdrawing groups on the aromatic ring, lead to a positive charge enhancement on the phosphorus atom. It was accompanied by a

decrease P-O_p bond length and a shielding effect on the phosphorus atom as can be seen in FIGURES 2 and 3. It can be rationalized in terms of the contributions of canonical structures I and III.

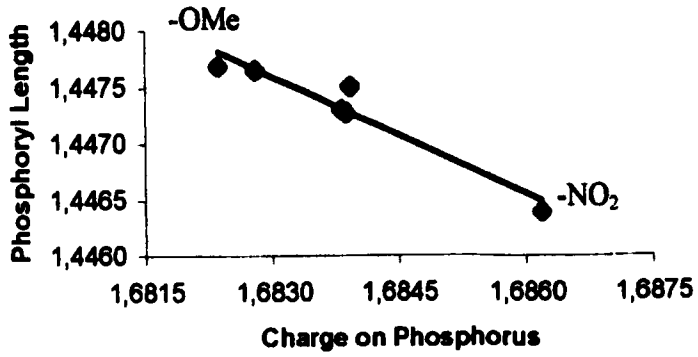


FIGURE 2 Relationship between the phosphoryl bond lengths and charge on phosphorus for aryl dihexyl phosphates (R^2=0.977 and slope= –0.151). R^2=0.927 and slope=-0.136 for diethyl phosphates. R^2=0.966 and slope=-0.122 for dibutyl phosphates

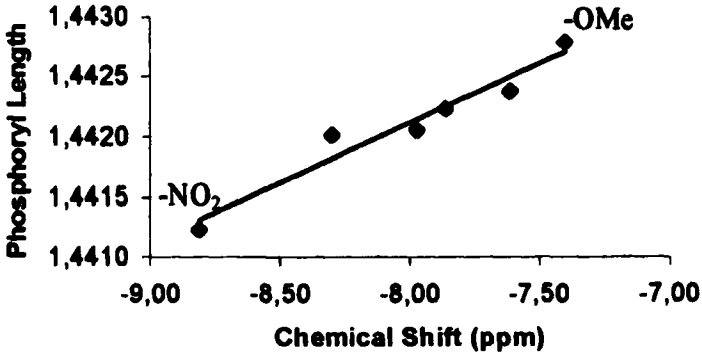


FIGURE 3 Relationship between the phosphoryl bond lengths and ^{31}P NMR chemical shift for aryl dihexyl phosphates (R^2=0.945 and slope=0.0010) R^2=0.892 and slope=0.0009 for diethyl phosphates. R^2=0.936 and slope=0.0009 for dibutyl phosphates

Electron withdrawing groups lead to the net charge on the phosphoryl and aryl oxygen atoms (O_p e O_{ar}, respectively) to lower negative values, accompanied by a decrease of the P-O_p bond length. This effect is in

accordance with the contribution of structure III. The canonical form II is disfavored in this case. It was observed, on other hand, an increase on the P-O_{ar} bond length. This effect is probably related to the contribution of structure III, disfavoring the form VI (FIGURES 4 and 5).

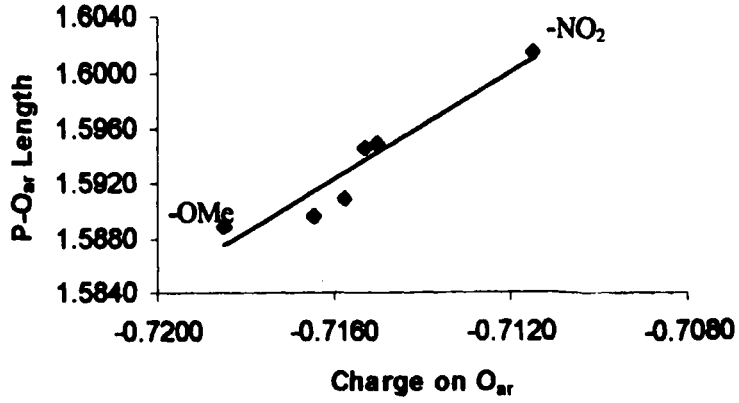


FIGURE 4 Relationship between the P-O_{ar} bond length and charge on aryl oxygen (O_{ar}) for aryl dihexyl phosphates (R^2=0.958 and slope=1.570) R^2=0.932 and slope=1.364 for diethyl phosphates. R^2=0.951 and slope=1.639 for dibutyl phosphates

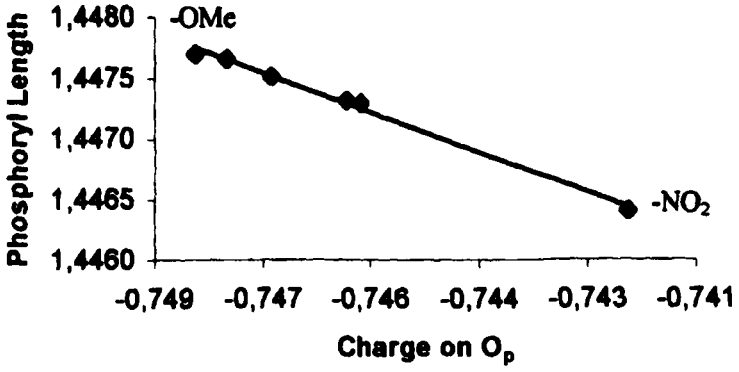


FIGURE 5 Relationship between the phosphoryl bond lengths and charge on phosphoryl oxygen (O_p) for aryl dihexyl phosphates (R^2=0.997 and slope= –0.226) R^2=0.994 and slope=-0.218 for diethyl phosphates. R^2=0.993 and slope=-0.221 for dibutyl phosphates

The geometric and electronic parameters are also related to the variation of ^{31}P NMR chemical shift, as can be seen in FIGURES 6–8.

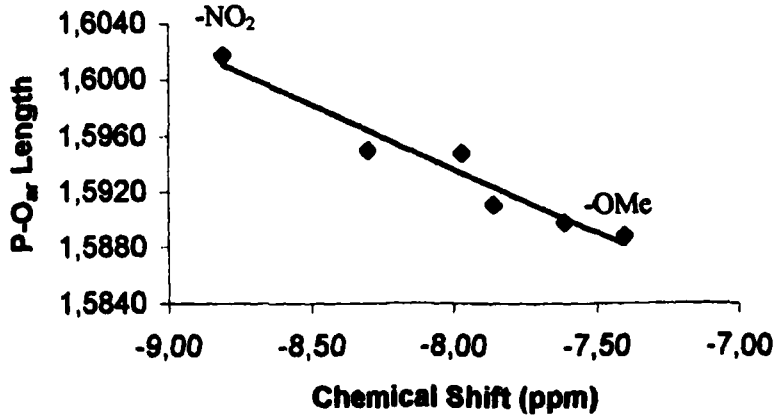


FIGURE 6 Relationship between the P-O_{ar} bond length and ^{31}P NMR chemical shift for aryl dihexyl phosphates (R^2=0.939 and slope=-0.0091) R^2=0.905 and slope= –0.0095 for diethyl phosphates. R^2=0.939 and slope=-0.0090 for dibutyl phosphates

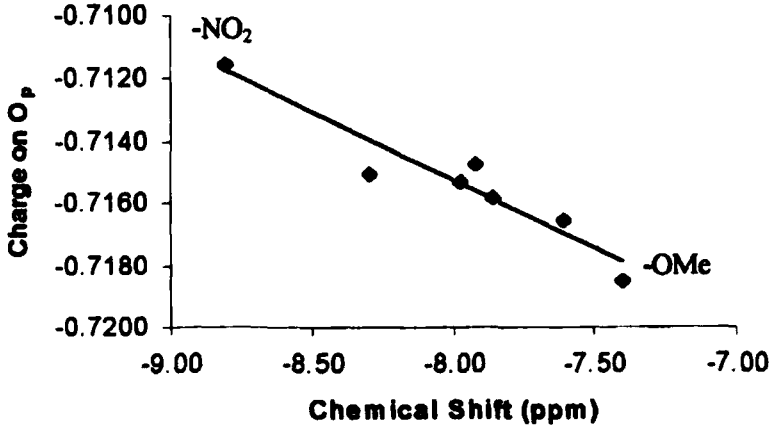


FIGURE 7 Relationship between charge on phosphoryl oxygen (O_p) and ^{31}P chemical shift for aryl dihexyl phosphates (R^2=0.934 and slope=-0.044) R^2=0.927 and slope=-0.0041 for diethyl phosphates. R^2=0.939 and slope=-0.0040 for dibutyl phosphates

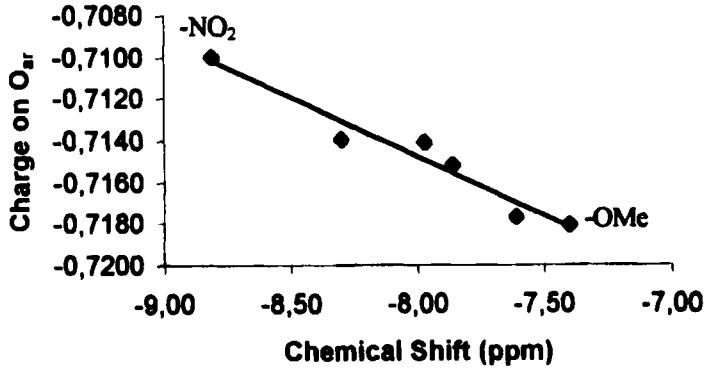


FIGURE 8 Relationship between the charge on aryl oxygen (O_{ar}) and the ^{31}P NMR chemical shift for aryl dihexyl phosphates (R^2 =0.9505 and slope=-0.0057) R^2=0.936 and slope=-0.0068 for diethyl phosphates. R^2=0.921 and slope=-0.0053 for dibutyl phosphates

The importance of structure (III) can also be checked by the changes in the C_{ar}-O_{ar} bond length due to the substituents on phenyl group. Again, this structure's contribution is higher for electron withdrawing groups (FIGURE 9)

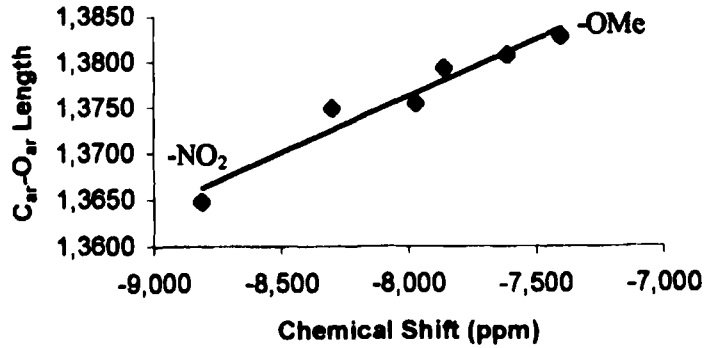


FIGURE 9 Relationship between the C-O bond length from aryl group (C_{ar}-O_{ar}) and the ^{31}P NMR chemical shift for aryl dihexyl phosphates (R^2=0.956 and slope=0.013) R^2=0.942 and slope=0.012 for diethyl phosphates. R^2=0.957 and slope=0.013 for dibutyl phosphates

The negative charge on the oxygen atom from alkoxy groups (P-O_{alk}) showed a tendency to decrease by electron withdrawing groups and the

P-O_{alk} bond length increase smoothly (FIGURE 10). It is an evidence of a slight back bond effect from the alkyl oxygens to the phosphorus atom (IV and V) (FIGURE 11).

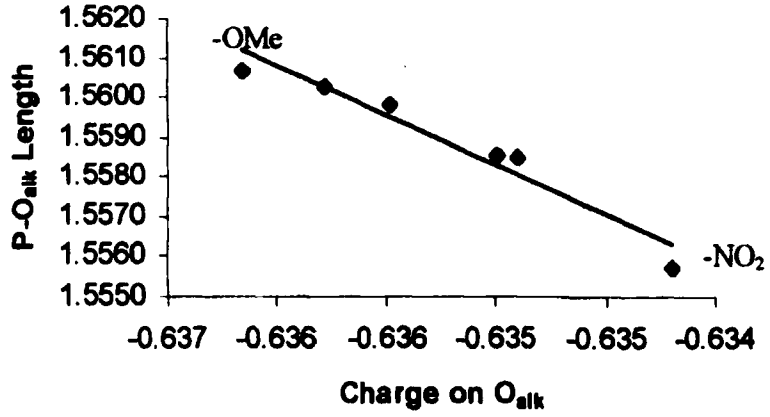


FIGURE 10 Relationship between the P-O_{alk} bond lengths and charge on alkyl oxygen (O_{alk}) for aryl dihexyl phosphates (R^2=0.977 and slope=-5.052) R^2=0.869 and slope=-2.756 for diethyl phosphates. R^2=0.956 and slope=-4.834 for dibutyl phosphates

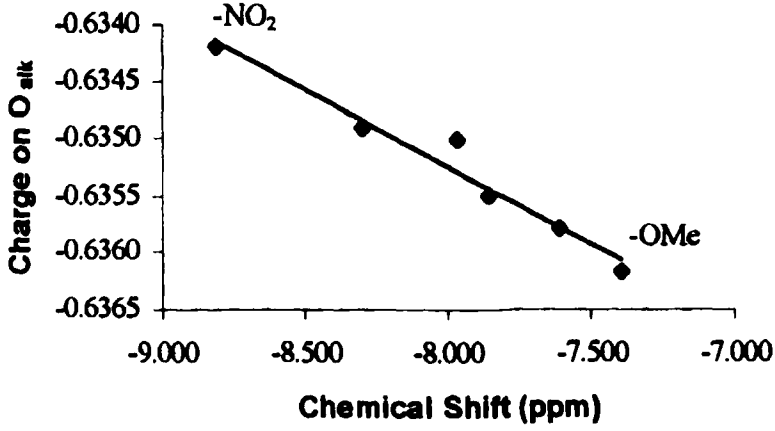


FIGURE 11 Relationship between the charge on alkyl oxygen (O_{alk}) and the ^{31}P NMR chemical shift for aryl dihexyl phosphates (R^2=0.965 and slope= -0.0007) R^2=0.925 and slope=-0.0014 for diethyl phosphates. R^2=0.953 and slope=-0.0008 for dibutyl phosphates

The electronic and structural changes observed point out that electron withdrawing groups lead to a shielding effect on the phosphorus atom as indicated by structures I, III, IV and V. On the other hand, electron-donating groups lead to the deshielding of the phosphorus atom. In this case, the importance of structures II and VI increases.

From the slopes modules, it is possible to estimate that the decreasing of the C_{ar}-O_{ar} bond (0.0123), favoring to structure III (related to a increasing shield on P atom), is a more important factor than the decrease P-O_{ar} bond (-0.0095), that is disfavoring structure VI (related to a decreasing shield on P atom) with electron withdrawing groups (TABLE II). A surprisingly minor slope was observed for the phosphoryl bond (0,0010).[3,5]

TABLE II Slopes from linear relation between some geometric and electronic parameters and ^{31}P NMR chemical shift

Observable versus $\delta^{31}P$	*Ethyl slope*	*Butyl slope*	*Hexyl slope*
P-O_p bond length	0.0009	0.0009	0.0010
P-O_{ar} bond length	–0.0095	–0.0090	–0.0091
2x P-O_{alk} bond length	0.0086	0.0076	0.0074
C_{ar}-O_{ar} bond length	0.0123	0.0127	0.0127
Charge on P	–0.0025	–0.0071	–0.0065
Charge on O_p	–0.0041	–0.0040	–0.0044
Charge on O_{ar}	–0.0068	–0.0053	–0.0057
Charge on O_{alk}	–0.0014	–0.0008	–0.0007

These results showed that all groups around the phosphorus atom probably influence the aryl phosphates chemical shift. The good linear correlation observed with the symmetry of the electron cloud model[4] in the structures analyzed in this work (R2=0.907, 0.933 and 0.956 for ethyl, butyl and hexyl series respectively) can be due to this fact. This model, however, showed a poor correlation when it was applied to the mono, di and triaryl phosphates simultaneously[5].

The observed relationship between geometric and electronic parameters suggests a possible influence of the oxigen p lone pair electrons and the pi-shielding region of the phenyl group on the ^{31}P NMR chemical shift. The electronic p lone pair population on the oxygens of the phosphoryl,

aryl and alkoxyl and the electronic pi population of the carbon atoms of the phenyl ring can be seen in FIGURES 12, 13, 14 and 15, respectively.

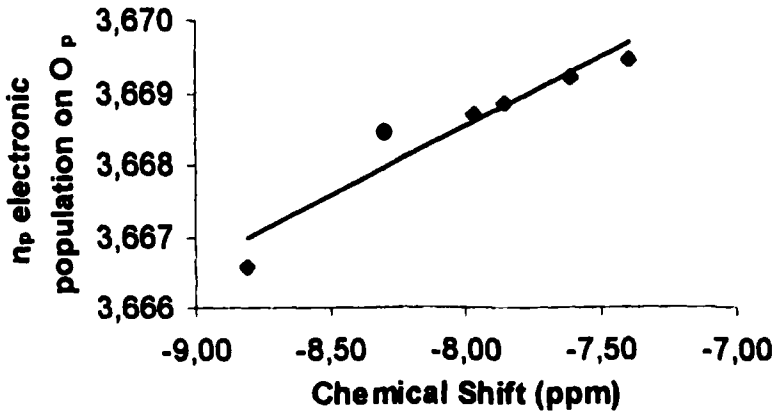


FIGURE 12 Relationship between the electronic population on the phosphoryl oxygen (O_p) and the ^{31}P NMR chemical shift for aryl dihexyl phosphates (R^2=0.913 and slope= 0.0019)

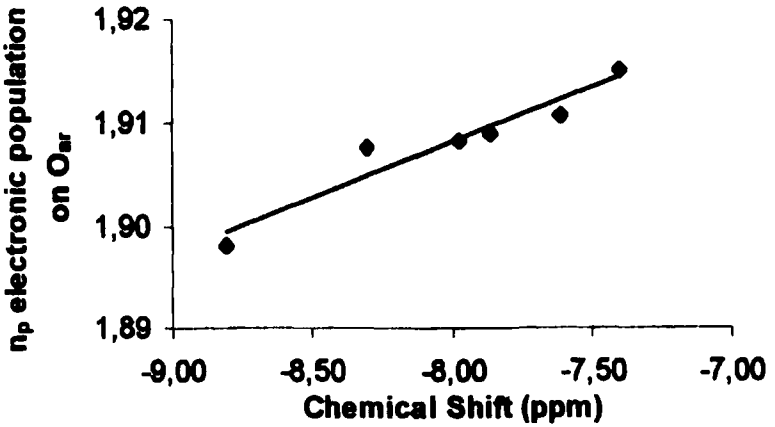


FIGURE 13 Relationship between the electronic population on the aryl oxyger (O_{ar}) and the ^{31}P NMR chemical shift for aryl dihexyl phosphates (R^2=0.921 and slope= 0.0106)

From the results shown on FIGURES 12, 13 and 14, the electronic population on the phosphoryl, aryl and alkoxyl p lone pair oxigens showed a

tendency to decrease by electron withdrawing groups. This behavior is in accordance with the the relationship between chemical shift and P-O_P, P-O_{ar}, C-O_{ar} and P-O_{alk} bond lengths shown in the FIGURES 3, 6, 9, 10 and 11. These results indicate that the shielding effect is mainly due to the backbonding of the phosphoryl and alkoxyl oxygens lone pairs with the electron withdrawing substituents in aryl group.

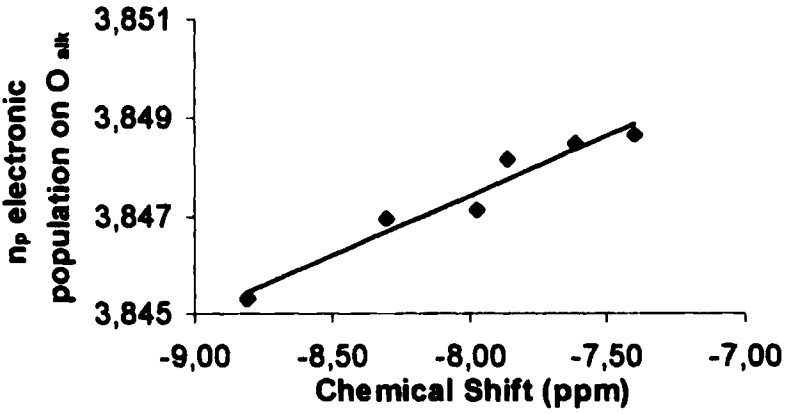


FIGURE 14 Relationship between the electronic population on the aryl oxygen (O_{alk}) and the ^{31}P NMR chemical shift for aryl dihexyl phosphates (R^2=0.945 and slope= 0.0025)

The electronic population on the aryl group was about five for all diaryl alkyl phosphates independent of the nature of the substituent (FIGURE 15), this observation suggests that the effect of delocalization of electrons from the phenyl group to the electron deficient phosphorus atom of the phosphoryl. This is in accordance with the chemical shift diminution observed when a comparison between mono, di and tri aryl phosphates, was carried out[5].

The HOMO and LUMO energy calculations presented in FIGURES 16 and 17, showed a larger variation on LUMO energies, when substituents are electron withdrawing. When these groups are electron donating, this variation is larger on HOMO energies. Owing to this behavior, the relationship between HOMO-LUMO energy gap and ^{31}P NMR chemical shift showed an increasing trend when the electron withdrawing and donating power of the substituent increased (FIGURE 18).

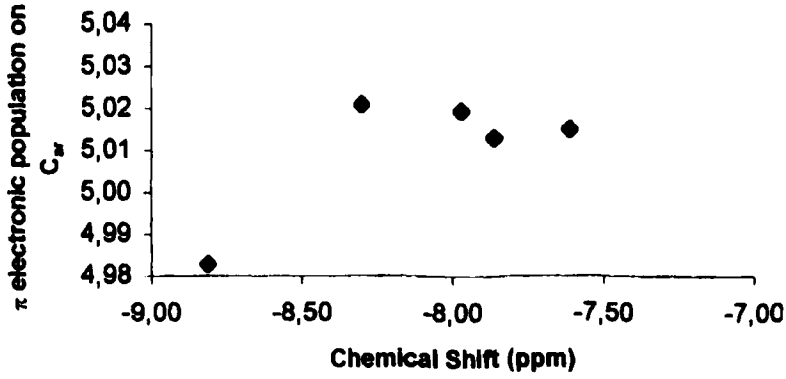


FIGURE 15 Relationship between the electronic population on carbon atom of the phenyl ring (C_{ar}) and the ^{31}P NMR chemical shift for aryl dihexyl phosphates

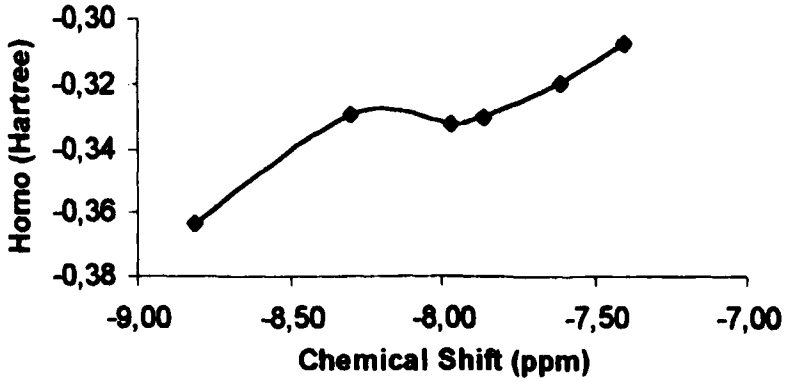


FIGURE 16 Relationship between HOMO energy and the ^{31}P NMR chemical shift for aryl dihexyl phosphates

Only strong electron donating or withdrawing groups cause a significant increase in the phosphorus' atom p character (FIGURE 19), indicating that this orbital is in some way related with the electronic delocalization effect. This effect is responsible for the shielding and deshielding relationships afore mentioned.

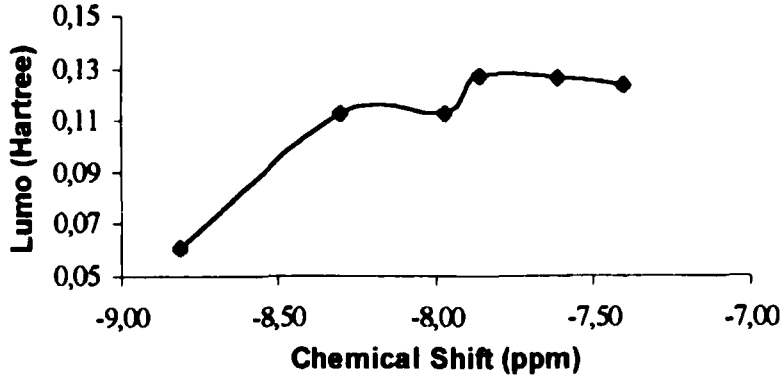


FIGURE 17 Relationship between HOMO energy and the ^{31}P NMR chemical shift for aryl dihexyl phosphates

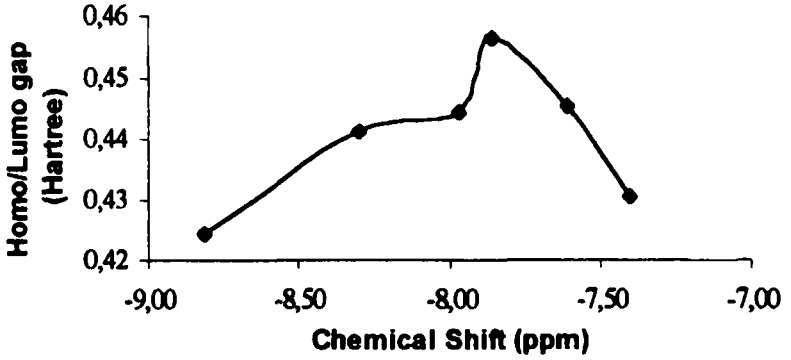


FIGURE 18 Relationship between the HOMO/LUMO gap and the ^{31}P NMR chemical shift for aryl dihexyl phosphates

COMPUTATIONAL PROCEDURE

The structures were optimized by the complete triple zeta base 6–311G* Hamiltonian in Hartree Fock level. When the electronic correlation effect was included at hybrid DFT level by the B3LYP model[9,10], the obtained results were not satisfactory. The theoretical absolute chemical shifts were

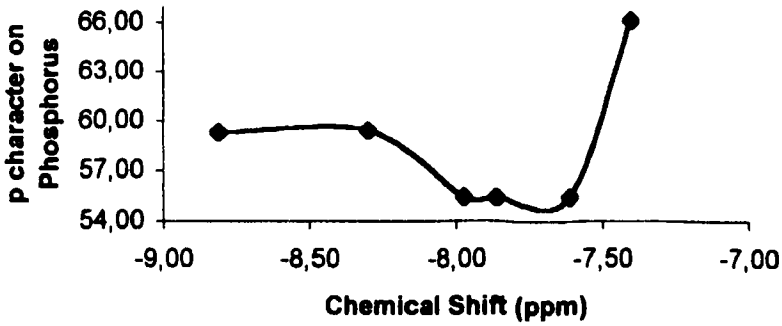


FIGURE 19 Relationship between p character on phosphorus and the ^{31}P NMR chemical shift for aryl dihexyl phosphates

calculated from GIAO[11] calculation in Hartree-Fock level. The relative values were obtained by fixing the theoretical and experimental dialkyl phenyl phosphate chemical shifts as being the same.

The optimized geometries and the respective chemical shifts were obtained from GAUSSIAN 94 software, running in a SP2 supercomputer.

References

[1] D. B. Chesnut, L. D. Quin, S. B. Wild, *Heteroatom Chem.*, **8**, 451–457 (1997).
[2] D. B. Chesnut, L. D. Quin, *Heteroatom Chem.*, **10**, 566–572 (1999).
[3] S. Hoz, E. J. Dunn, E. Buncel, R. A. Bannard and J. G. Purdon, *Phosphorus and Sulfur*, **24**, 321–326 (1985).
[4] Shusen Li, Xiugao Liao and Chengye Yan, *Phosphorus and Sulfur*, **48**, 69–75 (1990).
[5] J. F. Cajaiba da Silva, M. S. Pedrosa, H. T. Nakayama and C. Costa Neto, *Phosphorus and Sulfur*, **131**, 97–105 (1997).
[6] R.D. Johnson, R.M. Kastner, S.H. Larsen, E.E. Ose, US 4,482,488 (1984).
[7] N.W. Bischofberger, R.J. Jones, M.N. Arimill, M.N. Loiue, E.J. Prische, W.A. Lee US 5,798,340 (1998).
[8] J.P. Krise, J. Zygmunt, G. I. Georg and V. J. Stella, *J. Med. Chem.*, **42**,3094–3100, (1999).
[9] A. D. Back, *Phys. Rev. A*, **38**, 3098, (1988).
[10] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, **37**, 785–789, (1988).
[11] K. Wolinski, J.F. Hilton, P. Pulay, *J. Amer. Chem. Soc.*, **112**, 8251, (1990).