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Phosphazenes 3. Group Contributions to the Phosphorus-31 Chemical Shifts of Alkyl and Aryl Substituted Cyclotriphosphazenes

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The ^{31}P NMR spectra of 68 geminally di-substituted tetrachlorocyclotriphosphazenes have been analyzed. For the dialkyl complexes (I), partial chemical shift contributions can be calculated that allow very accurate prediction of chemical shifts. For the alkyl-halo complexes (II), several deviations from the predicted chemical shifts are observed. These can be rationalized in terms of steric interactions between the substituent groups. For the series of para-*substituted aryl phosphazenes (III), excellent correlation between the Hammett σ parameter and the ^{31}P NMR chemical shift is observed.*

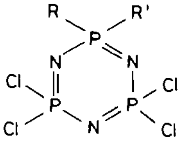
Introduction

Over the last few years, a number of new alkyl and aryl substituted chlorophosphazene compounds have been synthesized in our laboratory and elsewhere [1–4]. Several of these compounds are found to be precursors to a new series of alkylphosphazene polymers of both theoretical and technological importance [5]. While most of these compounds have been characterized by the use of ^{31}P NMR spectroscopy, no attempt has been made to interpret these data in terms of the steric and electronic effects of the substituent groups.

The NMR chemical shifts of phosphorus nuclei have been the subject of numerous theoretical [6, 7] and empirical treatments [8–11] and have been shown to be dependent on both the bond angle at phosphorus [12] and the electronegativity of the substituent groups. However, the application of quantum mechanical theory to the prediction and explanation of phosphorus chemical shifts requires numerous assumptions [6] and often simple empirical correlations are more useful [11].

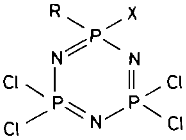
The idea of additive group contributions to the phosphorus NMR chemical shifts in trivalent phosphorus compounds was first suggested in 1956 by Van Wazer [13] and since then several papers have successfully applied this concept to both tri- [8] and tetra-coordinate [14] phosphorus.

In this paper, we explore the application of this additivity concept to a series of alkyl- and aryl-substituted phosphazene compounds of general formula I–III.



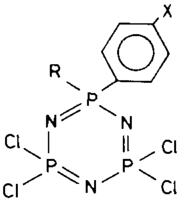
(I)

R' = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, C_3H_5.
R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, i-C_4H_9, t-C_4H_9, C_3H_5.



(II)

R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, t-C_4H_9.
X = H, Cl, Br, I.



(III)

R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, C_6H_5; X = H.
R = CH_3; X = H, Cl, F, CH_3, OCH_3, CF_3, $N(CH_3)_2$, $N(C_2H_5)_2$, C_6H_5, $C(CH_3)_3$.

Results and Discussion

The ^{31}P NMR chemical shift data for all compounds under consideration are listed in Table I. These compounds fall conveniently into three classes (I, II and III), both structurally and in terms of data analysis, and will be discussed as such in the following sections. Throughout this paper the discussion will be mainly concerned with the resonance position of the alkyl/aryl substituted phosphorus atoms, as the

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TABLE I. Calculated and Observed ^{31}P NMR Data for Alkyl/Aryl Phosphazenes.

Compound	Substituents	Chemical shift, ppm. PCl_2	PR_2 (observed)	PR_2 (calc.)
I	$R = CH_3, R' = CH_3$	18.0	35.7	35.6
I	$R = CH_3, R' = C_2H_5$	18.3	41.8	41.9
I	$R = CH_3, R' = n\text{-}C_3H_7$	18.2	39.6	39.6
I	$R = CH_3, R' = n\text{-}C_4H_9$	18.0	39.9	40.1
I	$R = CH_3, R' = i\text{-}C_3H_7$	17.9	46.1	46.4
I	$R = CH_3, R' = i\text{-}C_4H_9$	17.7	38.3	38.4
I	$R = CH_3, R' = t\text{-}C_4H_9$	18.1	50.4	50.3
I	$R = CH_3, R' = C_3H_5$	18.5	36.9	36.7
I	$R = C_2H_5, R' = C_2H_5$	19.2	48.1	48.2
I	$R = C_2H_5, R' = n\text{-}C_3H_7$	18.7	45.8	45.9
I	$R = C_2H_5, R' = n\text{-}C_4H_9$	18.7	46.3	46.4
I	$R = C_2H_5, R' = i\text{-}C_3H_7$	18.8	52.5	52.7
I	$R = C_2H_5, R' = i\text{-}C_4H_9$	18.3	44.7	44.7
I	$R = C_2H_5, R' = t\text{-}C_4H_9$	18.6	56.8	56.6
I	$R = C_2H_5, R' = C_3H_5$	19.2	43.1	43.0
I	$R = n\text{-}C_3H_7, R' = n\text{-}C_3H_7$	18.5	43.6	43.6
I	$R = n\text{-}C_3H_7, R' = n\text{-}C_4H_9$	18.5	44.1	44.1
I	$R = n\text{-}C_3H_7, R' = i\text{-}C_3H_7$	18.6	50.3	50.4
I	$R = n\text{-}C_3H_7, R' = i\text{-}C_4H_9$	18.0	42.4	42.4
I	$R = n\text{-}C_3H_7, R' = t\text{-}C_4H_9$	18.2	54.3	54.3
I	$R = n\text{-}C_3H_7, R' = C_3H_5$	18.9	40.9	40.7
I	$R = n\text{-}C_4H_9, R' = n\text{-}C_4H_9$	18.4	44.5	44.6
I	$R = n\text{-}C_4H_9, R' = i\text{-}C_3H_7$	19.0	51.1	50.9
I	$R = n\text{-}C_4H_9, R' = i\text{-}C_4H_9$	17.9	42.9	42.9
I	$R = n\text{-}C_4H_9, R' = t\text{-}C_4H_9$	18.2	54.8	54.8
I	$R = n\text{-}C_4H_9, R' = C_3H_5$	18.9	41.4	41.2
I	$R = C_3H_5, R' = C_3H_5$	19.3	37.8	37.8
I	$R = C_3H_5, R' = i\text{-}C_3H_7$	18.9	47.6	47.5
I	$R = C_3H_5, R' = i\text{-}C_4H_9$	18.5	39.8	39.5
I	$R = C_3H_5, R' = t\text{-}C_4H_9$	19.2	51.3	51.4
II	$R = CH_3, X = H$	17.6	13.8	13.6
II	$R = C_2H_5, X = H$	18.4	20.2	19.9
II	$R = n\text{-}C_3H_7, X = H$	19.0	17.4	17.6
II	$R = n\text{-}C_4H_9, X = H$	19.4	17.9	18.1
II	$R = i\text{-}C_3H_7, X = H$	18.4	26.5	26.5[a]
II	$R = t\text{-}C_4H_9, X = H$	18.4	32.3	32.3[a]
II	$R = CH_3, X = Cl$	21.3	39.2	39.7(39.2)[a]
II	$R = C_2H_5, X = Cl$	21.7	46.0	46.0
II	$R = n\text{-}C_3H_7, X = Cl$	21.3	43.7	43.7
II	$R = n\text{-}C_6H_9, X = Cl$	21.4	44.2	44.2
II	$R = i\text{-}C_3H_7, X = Cl$	21.7	51.8	50.5(51.8)[a]
II	$R = t\text{-}C_4H_9, X = Cl$	21.8	57.1	54.4(57.1)[a]
II	$R = CH_3, X = Br$	21.1	24.4	28.4(24.4)[a]
II	$R = C_2H_5, X = Br$	21.6	34.8	34.7
II	$R = n\text{-}C_3H_7, X = Br$	21.7	32.4	32.4
II	$R = n\text{-}C_4H_9, X = Br$	21.5	32.7	32.9
II	$R = i\text{-}C_3H_7, X = Br$	21.6	43.6	43.6[a]
II	$R = t\text{-}C_4H_9, X = Br$	21.7	51.4	51.4[a]
II	$R = CH_3, X = I$	21.0	−16.3	−16.3[a]
II	$R = C_2H_5, X = I$	21.3	−0.7	−0.6
II	$R = n\text{-}C_3H_7, X = I$	21.0	−2.9	−2.9
II	$R = n\text{-}C_4H_9, X = I$	21.0	−2.3	−2.4
II	$R = i\text{-}C_3H_7, X = I$	21.3	16.3	16.3[a]
II	$R = t\text{-}C_4H_9, X = I$	20.3	26.0	26.0[a]
III	$R = CH_3, X = H$	18.6	29.0	28.8
III	$R = C_2H_5, X = H$	18.9	35.4	35.1
III	$R = n\text{-}C_3H_7, X = H$	18.7	32.5	32.8
III	$R = n\text{-}C_4H_9, X = H$	18.8	33.0	33.3
III	$R = C_6H_5, X = H$	18.3	21.4	22.0
III	$R = CH_3, X = Cl$	19.0	28.3	
III	$R = CH_3, X = F$	18.7	28.4	
III	$R = CH_3, X = CH_3$	18.7	29.4	
III	$R = CH_3, X = OCH_3$	18.6	29.3	
III	$R = CH_3, X = CF_3$	19.1	27.7	
III	$R = CH_3, X = N(CH_3)_2$	18.3	30.0	
III	$R = CH_3, X = N(C_2H_5)_2$	18.2	30.0	
III	$R = CH_3, X = C_6H_5$	18.8	29.1	
III	$R = CH_3, X = C(CH_3)_3$	18.3	29.2	

[a] Chemical shifts calculated using eqn. 1 and bulk coefficients (Table III).

resonance for the PCl_2 groups in all the compounds under consideration always falls between 18–22 ppm and shows little or no consistent chemical shift variation with changes in the organic substituents.

1,1-Dialkyl Substituted Compounds (I) [1]

Several general observations can be made upon initial inspection of the data for these compounds. First, fairly large chemical shift differences occur in the resonance position of the alkylated phosphorus atom upon minor changes in the substituent groups. For example, the difference in the resonance position between the 1,1-dimethyl compound (I, $R = R' = CH_3$, at 35.7 ppm) and the 1-methyl-1-ethyl complex (I, $R = CH_3$; $R' = C_2H_5$, at 41.8 ppm) is 6.1 ppm. This is significantly larger than the difference found in simple quaternary triphenylphosphonium salts [15].

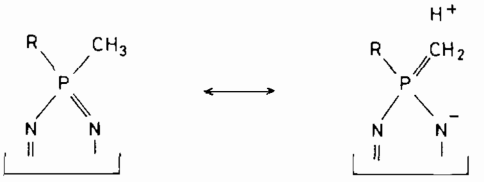
The ^{31}P NMR chemical shift for the alkylated phosphorus atom appears to show no correlation with the Taft σ constants for the various alkyl groups. However, a partial contribution towards the total chemical shift of this phosphorus atom can be calculated for each alkyl group. These data are listed in Table II. Use of these partial chemical shift contributions allows for the prediction of the chemical shift positions of the NMR resonance of the alkylated phosphorus atom in every dialkyl compound with very high accuracy, generally within 0.1 ppm. (The worst case is 0.3 ppm!) For all the dialkyl compounds, the average error is less than 0.5%. A plot of observed chemical shift versus calculated chemical shift has a correlation coefficient for all the data of 0.9997. These predictions are far more accurate than for any other series of quadruply connected phosphorus compounds that have previously been considered. For the quaternary phosphonium salts,

TABLE II. Partial Chemical Shift Contributions for Alkyl/Aryl Phosphazenes.

CH_3	17.8 ppm	Allyl	18.9 ppm
C_2H_5	24.1 ppm	Phenyl	11.0 ppm
n-C_3H_7	21.8 ppm	H	−4.4 ppm
n-C_4H_9	22.3 ppm	Cl	21.9 ppm
i-C_3H_7	28.6 ppm	Br	10.6 ppm
i-C_4H_9	20.6 ppm	I	−24.7 ppm
t-C_4H_9	32.5 ppm		

$[R_4P]Br$, chemical shifts can be calculated [14] to an average error of ~4.0% (a plot of observed versus calculated chemical shifts has a correlation coefficient of 0.98); whereas, for compounds such as $R_3P{=}O$, no partial chemical shift contributions for the organic substituents could be calculated [13].

As in previous work [8], it should be noted that the order of the partial chemical shift contributions for various groups is $CH_3 < C_2H_5 <$ i-$C_3H_7 <$ t-C_4H_9. This is the reverse order from that expected by simple inductive effect arguments. This ordering of groups was previously rationalized in terms of hyperconjugation between the α protons of the alkyl group and the phosphorus d orbitals, and mathematically based arguments have been presented to explain the phenomenon [8]. In phosphazene compounds, hyperconjugation would suggest a structure such as IV, which would not be totally unreasonable, since the α protons in alkylated phosphazene compounds are known to be acidic [16, 17]. Other possible effects which could be used to explain the chemical shift variations include changes in the exocyclic bond angle between the alkyl groups [12], or variation of the electron density within the phosphazene ring [18]. Changes in the exocyclic bond angle at phosphorus seems unlikely in these compounds; however, this effect will be discussed further in a later section. Variation in the electron density within the phosphazene ring can be conveniently used to rationalize the chemical shift variations by consideration of the 'island' theory of phosphazene bonding [19]. The argument is as follows: The presence of an electron-donating alkyl group at one end of the P–N–P island will allow electron density to drift towards the other end of the island. The greater the electron donating ability of the alkyl group, the greater this electron drift; this effectively deshields the alkylated phosphorus atom. The argument is also supported by the resonance position for the PCl_2 groups in this series of compounds. These resonances always fall between 17.7 and 19.3 ppm, upfield from the resonance for $N_3P_3Cl_6$ at 19.8 ppm; this shift clearly indicates that some degree of shielding is achieved by the drift of electron density towards the PCl_2 groups.



(IV)

1-Alkyl-1-Halo/Hydrido Compounds II [2, 3]

For each series of these compounds where the X group is the same, the chemical shift trends, due to changes in the alkyl group, are similar to the 1,1-dialkyl series of compounds. Also, for the series of compounds with the same alkyl group, the effect of the halogen atom on the chemical shift of the alkylated phosphorus is quite large. For example, the chemical shift difference between the mono-n-propylpentachloro compound (II, R = n-C_3H_7; X = Cl, 43.7 ppm) and the 1-n-propyl-1-iodo compound (II, R = n-C_3H_7; X = I, −2.9 ppm) is 46.6 ppm.

However, when attempts are made to calculate partial chemical shift contributions for the halogen or hydride groups, several problems are encountered. The partial chemical shift values for the alkyl groups that were determined for the dialkyl compounds were used, (Table II), and thus a partial chemical shift contribution for the halogen/hydride group was determined. The data (calculated *vs.* found) for the monoalkylpentachloro compounds (average error ~4.0%) and the hydrido compounds (average error ~7.0%) fitted fairly well. However, for the bromo- and iodo-derivatives these data did not fit well at all. In an attempt to rationalize these deviations, the steric, electronic, and hyperconjugative effects of the substituent groups were examined. Electronic effects can be ruled out, as they should be the same for each series of halogens. Any type of hyperconjugative effect should be taken care of by the alkyl group contribution. This only leaves steric interactions. Various molecular models and structural diagrams (see experimental section) were made to determine the stereochemical interactions of the substituent groups about the substituted phosphorus atom. These were quite informative. They indicated that for the simple n-alkyl substituents the exocyclic bond angle for all classes of compounds could readily be ~105°, similar to that determined for many dialkyl phosphazenes [18]. However, the i-propyl and t-butyl groups interacted quite strongly with the bromo- and iodo-substituents at this angle. (The minimum bond angle for the t-butyl-iodo compound for no interaction was found to be ~118°).

The ^{31}P NMR data were then reassessed in terms of the above findings and only the n-alkyl compounds were used to calculate the partial chemical shift contributions for the halogen/hydride substituents. These data are listed in Table II. The ^{31}P NMR chemical shifts for the methyl, i-propyl and t-butyl compounds can now be rationalized by the use of eqn. (1):

Chemical Shift Observed = Partial Shift Contribution for Halogen + (Partial Shift Contributions for Alkyl) X (Bulk Coefficient.) (1)

The partial chemical shift contributions are those listed in Table II. The bulk coefficient essentially describes the degree of interaction (variation in exocyclic bond angle?) between the alkyl group and the halogen [20]. The various bulk coefficients are listed in Table III. Interestingly, the bulk coefficients for the methyl compounds are all less than one, which could indicate a possible closure of the CH_3–P–X bond angle below 105°. These coefficients can be conveniently used to correct the NMR data for the halo-/hydrido compounds; however, more x-ray crystallographic studies must be undertaken to determine if these bulk coefficients have any real significance.

1-Alkyl-1-Aryl-Compounds III [4]

For the series of compounds III (R = CH_3, C_2H_5, n-C_3H_7 and n-C_4H_9, X = H), a partial chemical shift value for the aryl group can be determined in the same manner as described above for the dialkyl compounds, (I). The accuracy (calculated *vs.* found) in these cases is ~2.0%. The series of compounds III (R = CH_3; X = H, Cl, F, CH_3, OCH_3, CF_3, $N(CH_3)_2$, $N(C_2H_5)_2$, C_6H_5) show a marked variation in their ^{31}P NMR spectra, dependent on the nature of the para-substituent on the aromatic ring. For these compounds, there appears to be a good correlation between the chemical shift and the simple Hammett σ para parameter [21] as shown in Fig. 1. For these data, the correlation coefficient is 0.963, far better than that found for a series of triaryl phosphines [11]. These data clearly indicate a strong interaction of the aromatic ring with the phosphazene moiety; however, the exact nature of this interaction is unclear at the present time and is currently under investigation [4].

TABLE III. Bulk Coefficients for Alkylhalophosphazenes.

Compound	Substituents	Bulk coefficient
II	R = i-C_3H_7, X = H	1.08
II	R = t-C_4H_9, X = H	1.13
II	R = CH_3, X = Cl	0.97
II	R = i-C_3H_7, X = Cl	1.05
II	R = t-C_4H_9, X = Cl	1.08
II	R = CH_3, X = Br	0.78
II	R = i-C_3H_7, X = Br	1.15
II	R = t-C_4H_9, X = Br	1.26
II	R = CH_3, X = I	0.47
II	R = i-C_3H_7, X = I	1.43
II	R = t-C_4H_9, X = I	1.56

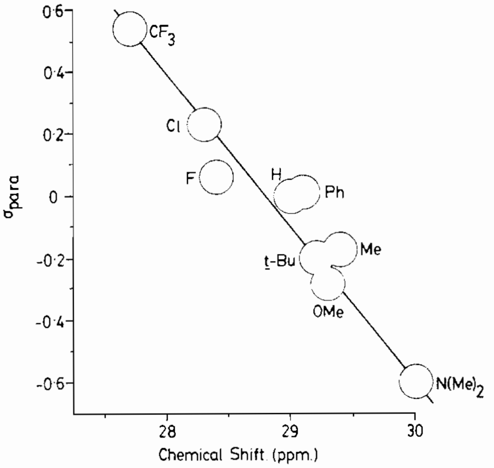


Fig. 1. Hammett σ constants *vs.* ^{31}P chemical shift for para-substituted aryl phosphazenes, (III).

Experimental

All compounds were synthesized by previously reported procedures [1–4]. Phosphorus-31 NMR spectra were run on a JEOL 200 supercon spetrometer operating at 80 MHz in the Fourier Transform mode. Samples were 10% by weight in chloroform-d and were referenced internally to a capillary of 85% phosphoric acid.

Structural diagrams of the halogen compounds (II) were drawn using standard bond angles and distances as determined by X-ray crystallography. Further details and copies of the diagrams are available from the author.

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