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ARYL-SUBSTITUTED FLUOROPHOSPHAZENES

VIII *. ^{13}C NUCLEAR MAGNETIC RESONANCE PARAMETERS FOR PHENYL-SUBSTITUTED FLUOROCYCLOTRIPHOSPHAZENES

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Summary

The ^{13}C NMR spectra of the series of compounds $P_3N_3F_{6-n}(C_6H_5)_n$ (n = 1, 2, 4) are recorded and discussed. The *para* carbon chemical shift indicates that the phosphazene ring exerts a moderate to strong electron withdrawing effect on the phenyl ring. Known correlations of ^{13}C chemical shifts with electron withdrawing parameters allow assignment of σ^+ values for $P_3N_3F_{6-n}(C_6H_5)_{n-1}$ from 0.42 (n = 4) to 0.74 (n = 1). Possible mechanisms for the perturbation of the phenyl ring are discussed. The phosphorus—carbon coupling constants to the C-2 (*ortho*) carbon are related to the nature of the substituents on the phosphorus atom in question.

Introduction

There has been considerable interest in the interactions of organic centers of π electron density with Main Group elements in high formal oxidation states e.g. Si(IV) and P(V) [2,3]. Recently we reported the ^1H NMR spectra of a series of phenyl substituted fluorocyclotriphosphazenes and concluded that the cyclotriphosphazene moiety was a strong electron-withdrawing group with respect to the phenyl ring [4]. Unfortunately, ^1H chemical shifts are subject to a wide variety of shielding mechanisms and therefore a better probe of the electronic interactions in these is desirable. Fluorinated monoaryl fluorocyclophosphazenes have been examined by ^{19}F NMR spectroscopy [5]. The results of this investigation are compatible with the results of the ^1H NMR spectroscopic studies. However, the interpretation of ^{19}F chemical shifts in fluoroaryl derivatives is a subject of some controversy [6,7]. Since ^{13}C NMR parameters are good probes to π electron density in aryl rings [8,9] and since there has been considerable recent interest in the ^{13}C NMR spectra of organophosphorus compounds [10,11], we

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* For part VII see ref. 1.

have chosen to investigate the ^{13}C NMR spectra of a series of phenyl substituted fluorocyclotriphosphazenes, $P_3N_3F_{6-n}(C_6H_5)_n$ (n = 1, 2, 4).

Experimental

Materials

The phenyl-substituted fluorocyclotriphosphazenes were prepared and purified by previously reported procedures [13].

Measurements

Natural abundance, proton noise-decoupled ^{13}C NMR spectra were recorded at 22.63 MHz in the Fourier transform mode on a Bruker WH90 spectrophotometer equipped with a Nicolet 1080 computer. Solution concentrations ranged from 0.5 to 3.8 mol% (approximately 9% by weight) in deuterochloroform. Shifts were measured from the solvent resonance and converted to a scale relative to benzene using the reported shift of benzene in chloroform [8].

Results

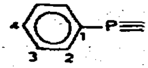
The ^{13}C NMR spectra of the phenyl substituted fluorocyclotriphosphazenes typically show three doublets with decreasing splitting as one goes downfield. Thus the shifts of the carbon atoms *ortho* (C-2), *meta* (C-3) and *para* (C-4) to the phosphazene moiety are easily assigned. These data are summarized in Table 1. The resonance due to C-1 was only detected in $P_3N_3F_5C_6H_5$. The low intensity of the C-1 signal can be ascribed to lack of nuclear Overhauser enhancement and possibly to slow relaxation of the directly bonded phosphorus atom [13]. The spectra of the *cis* and *trans* diphenyl derivatives, 1,3-$P_3N_3F_4(C_6H_5)_2$, show an additional line located within each of the C-2 and C-3 doublets. Since there is no reasonable assignment of these signals to the molecules in question, it is assumed that they arise from an impurity (possibly a phenoxy substituted cyclotriphosphazene).

The concentrations of the solutions were chosen such that contributions to

TABLE 1

SELECTED ^{13}C NMR PARAMETERS OF PHENYL FLUOROCYCLOTRIPHOSPHAZENES

Compound	Chemical shifts [a]			Coupling constants [c]		
	C-2 [b]	C-3	C-4	J(P—C-2)	J(P—C-3)	J(P—C-4)
$P_3N_3F_5(C_6H_5)$ [d]	0.6	2.2	5.8	17.1	12.2	2.4
cis-1,3-$P_3N_3F_4(C_6H_5)_2$	0.4	2.1	5.2	17.1	12.2	*e*
trans-1,3-$P_3N_3F_4(C_6H_5)_2$	0.4	2.1	5.1	17.1	12.2	2.4
1,1-$P_3N_3F_4(C_6H_5)_2$	0.4	2.0	4.2	14.0	11.6	2.4
1,1,3,3-$P_3N_3F_2(C_6H_5)_4$	—0.1	2.1	2.9	14.0	11.0	*e*

[a] Parts per million relative to benzene; positive shift downfield. [b]  [c] Hz. [d] C-1 = —4.7 ppm; J(P—C-1) = 142.4. [e] Line broadened indicating unresolved coupling.

the chemical shift due to solvent or high solute concentration were minimized [9,14]. In line with this expectation, variation in concentration did not produce any significant changes in the NMR parameters with the exception of a rare, random 1 Hz change in *J*(P—C-3) and *J*(P—C-2).

Discussion

Examination of the ^{13}C chemical shifts for $P_3N_3F_5C_6H_5$ allows one to conclude that the phosphorus atom in this system exerts a strong perturbation on the phenyl ring. The ^{13}C chemical shifts in substituted benzene rings have often been discussed in terms of substituent modification of the aryl π system [8]. In fact, the *para* carbon atom chemical shift in monosubstituted benzene derivatives has been successfully correlated to the total and π charge densities at the *para* carbon atom (as calculated by the CNDO/2 method) [9]. The $P_3N_3F_5$ and NO_2 substituents give the same *para* carbon atom chemical shift so they may be assumed to perturb the aryl π system to a similar degree. The observation of a strong electron withdrawing effect of the $P_3N_3F_5$ function, as measured by ^{13}C NMR, is in agreement with earlier ^{19}F [5] and ^{1}H [4] measurements. The magnitude of this electron effect may be expressed by the (familiar) σ^+ constants [15]. A value of σ^+ of approximately 0.74 can be obtained from a correlation of σ^+ vs. *para* carbon chemical shifts [9].

The mechanism of the modification of the aryl π charge density is a more subtle problem [16]. Substituent effects which are manifested at the *para* carbon atom are commonly ascribed to mesomeric interactions. However, the ^{13}C NMR parameters for $P_3N_3F_5C_6H_5$ are very similar to those observed for $C_6H_5POCl_2$ [10]. The mesomeric effects of phosphine oxides have been estimated to be low e.g. $\sigma_R^0 \simeq 0.07$ which corresponds to a weak resonance acceptor [17]. Therefore, one should consider the possibility that coulombic effects (π inductive and field effects) play a significant role in these systems. The implication of coulombic effects in the ^{13}C NMR chemical shifts for other Group V aryl derivatives should be noted. On going from phosphines to phosphonium ions the *para* carbon resonance is shifted approximately 7 ppm downfield [11] and the *para* carbon chemical shift in $(C_6H_5)_3SbBr_2$, a system where mesomeric effects would be expected to be minimal, is 4.3 ppm downfield from benzene [18]. Further work on the nature of the electron withdrawing effect of the fluorophosphazene ring will be the subject of a future communication.

In considering the entire series, $P_3N_3F_{6-n}(C_6H_5)_n$ ($n = 1, 2, 4$), one can see a sharp drop in the electron withdrawing effect of the phosphazene ring as the electronegative fluorine atoms are replaced by phenyl groups. The *para* carbon atom chemical shifts range from +5.8 ppm ($P_3N_3F_5C_6H_5$) to +2.9 ppm (1,1,3,3-$P_3N_3F_2(C_6H_5)_4$). The estimated σ^+ constants are as follows: 1,3-$P_3N_3F_4(C_6H_5)_2$, 0.66; 1,1-$P_3N_3F_4(C_6H_5)_2$, 0.57; 1,1,3,3-$P_3N_3F_2(C_6H_5)_4$, 0.42. This trend is consistent with either coulombic or mesomeric perturbation of the aryl π system. The successive removal of fluorine atoms decreases the positive charge at the phosphorus center hence less coulombic effects; however, concomitantly the phosphorus *d* orbitals will expand [19], overlap with the small carbon orbitals will become less significant and mesomeric interaction will diminish. In any case, substitution at a distant site on the phosphazene ring can produce significant changes in the *para* carbon chemical shifts thus demonstrating the effective transmission of electronic effects throughout the phosphazene ring. Similar conclusions have been drawn from consideration of phosphorus—phosphorus coupling constants in these compounds [20].

The observation of essentially identical *para* carbon chemical shifts in both *cis*- and *trans*-1,3-$P_3N_3F_4(C_6H_5)_2$ contrasts with the substantively different ^1H NMR shifts observed for the *para* protons in these compounds [4]. The difference in *para* proton chemical shifts was ascribed to differing electronic effects between the two isomers but the ^{13}C data clearly show this is not the case. The difference in ^1H shifts probably reflects a solvation phenomenon and demonstrates the difficulties in dealing with ^1H chemical shifts where a wide variety of shielding mechanisms are possible.

The value of J(P—C-1) in $P_3N_3F_5C_6H_5$ is quite high for aryl phosphorus derivatives but is comparable to the value observed for $C_6H_5POCl_2$ [10]. The value of J(P—C-2) in the series of compounds under consideration fall into two groups i.e. a $\equiv PFC_6H_5$ center has J(P—C-2) $\simeq$ 17 Hz while a $\equiv P(C_6H_5)_2$ center exhibits a J(P—C-2) $\simeq$ 14 Hz. Similar behavior has been observed for J(PCCH) [4]. The origin of this effect could lie in % *s* character (smaller bond angle in a $\equiv P(C_6H_5)_2$ center) or in a greater positive charge in a $\equiv PF(C_6H_5)$ center. Whatever the causes, the magnitude of J(P—C-2) clearly has diagnostic value in structure assignment.

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