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Aryl-Substituted Fluorophosphazenes. VI. Hydrogen-1 Nuclear Magnetic Resonance Parameters for Phenyl-Substituted Fluorocyclotriphosphazenes[1]

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The proton nmr parameters of a series of arylfluorocyclotriphosphazines, $P_3N_3F_{6-n}Ar_n$ (n = 1, 2, 4; Ar = phenyl, [3,5-$^2H_2$]-phenyl), have been recorded and discussed. The chemical shift of the para proton in $P_3N_3F_5C_6H_3D_2$ suggests that the phenyl group is subject to strong conjugative electron withdrawal by the cyclotriphosphazene ring. The extent of this interaction decreases with increased degree of substitution on the phosphazene ring. Differences in the chemical shifts of both the ortho and para protons between cis and trans isomers of 1,3-$P_3N_3F_4Ar_2$ are observed and discussed. Variations in the magnitude of the phosphorus–ortho proton coupling constant are also discussed. Substantive solvent effects were noted when spectra were obtained using benzene-d_6 as the solvent.

Introduction

In recent years, there has been extensive discussion of the possibility of conjugative interactions in aryl-substituted silicon compounds[2] and to a lesser extent in aryl-substituted phosphorus(V) compounds. Early reports of the electronic spectra of phenylchlorocyclotriphosphazenes indicated no variation in the spectra with structural changes.[3] Recent work has shown some variation in intensity in the phenyl bands of a series of phenyl-substituted cyclotriphosphazenes.[4] The phosphorus-31 nmr spectra of aryl-substituted phosphorus(V) compounds have been interpreted as indicating no aryl–phosphorus π interaction.[5] The opposite conclusion has been arrived at from a consideration of nuclear quadrupole resonance data.[6] While the present study was in progress, a report of ^{19}F nmr study of perfluoro- and monofluorophenyl derivatives of the type $P_nN_nF_{2n-1}Ar$ (n = 3–8) appeared.[7] The results of this study indicated strong inductive and conjugative electron withdrawal by the fluorophosphazene ring.

Since the phosphazene ring bonding is strongly influenced by the electronegativity of the exocyclic group,[8] it would be of interest to see if similar results were obtained with the unfluorinated phenyl group. Furthermore, it is of interest to see how the degree and stereochemistry of phosphazene ring substitution affects the electronic structure of the phenyl group. Thus, we have chosen to study the ^1H nmr spectra of a series of phenyl-substituted fluorocyclotriphosphazenes, $P_3N_3F_{6-n}Ar_n$ (n = 1, 2, 4; Ar = phenyl and [3,5-$^2H_2$]phenyl).

Experimental Section

Materials. Hexafluorocyclotriphosphazene[9] and phenyl-substituted fluorocyclotriphosphazenes[10-12] were prepared by previously reported procedures. The preparation of [3,5-$^2H_2$]phenyllithium follows established procedures.[13] Nitrobenzene-d_5 and benzene-d_6 were obtained from Stohler Isotopes, Inc. All other reagents and solvents were reagent grade and used without further purification.

Synthesis. The introduction of $C_6H_3D_2$ and C_6D_5 substituents onto the cyclotriphosphazene ring is based on known procedures for the corresponding addition of a phenyl group.[10-12] The synthetic sequence employed is summarized as in Scheme I.

Measurements. Initial measurements on the phenyl-substituted fluorocyclotriphosphazenes were performed on a Varian A-60 spectrophotometer equipped with a Varian 6058A homonuclear spin decoupler. The spectra were obtained in benzene-d_6 with 1% TMS as an internal standard. Measurements were made at several concentrations and extrapolated to infinite dilution. Measurements on the *m*-deuteriophenylfluorocyclotriphosphazenes were performed on a JEOL JNM-MH-100 spectrophotometer operating at 100 MHz. Spectra were obtained on approximately 5% solutions. The solutions were diluted and the spectra were recorded again to check for any concentration dependence. Measurements in benzene-d_6 and hexafluorobenzene were relative to internal benzene while those in cyclohexane were relative to internal TMS. The data obtained for the cyclohexane solutions were converted to benzene scale by using a conversion factor obtained by measurement of a dilute benzene solution in cyclohexane.

Results

The ^1H nmr spectra of the phenylfluorocyclotriphosphazenes contain two basic multiplets in a ratio of 2:3. The separation between multiplets is sensitive to the solvent employed with benzene-d_6 giving the largest effect. Similar results have been observed with other organophosphorus compounds.[14] Irradiation of the upper-field multiplet reduces the low-field multiplet to a doublet of *ca.* 15 Hz which can be assigned to the ortho protons coupled with the phosphorus atom. First-order analysis of the ortho proton peaks gives the same results as the decoupling experiment. The upper-field peaks are not simplified by decoupling or susceptible to first-order analysis. The chemical shifts of the ortho protons decrease with concentration until a concentration range of 10–20% is reached. No variation is observed with continued dilution.

In order to obtain para proton chemical shifts, the phosphazene derivatives with the phenyl group deuterated in the meta positions were prepared. The resulting nmr spectra consist of a low-field doublet and a singlet further upfield. Although some line broadening is expected from deuterium coupling, the line widths are not much broader than that of benzene under the same conditions. The ortho proton data are comparable to those obtained from the C_6H_5 derivatives. The nmr data obtained may be found in Table I.

Discussion

Detailed studies of the proton chemical shifts in monosubstituted benzenes indicate that, while the ortho proton shifts

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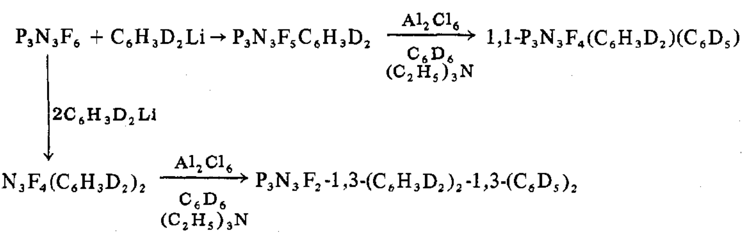
Scheme I



$$\begin{tikzcd}
P_3N_3F_6 + C_6H_3D_2Li \arrow[r] & P_3N_3F_5C_6H_3D_2 \arrow[d, "2C_6H_3D_2Li"] \arrow[r, "Al_2Cl_6"', "C_6D_6 \\ (C_2H_5)_3N"] & 1,1\text{-}P_3N_3F_4(C_6H_3D_2)(C_6D_5) \\
 & 1,3\text{-}P_3N_3F_4(C_6H_3D_2)_2 \arrow[r, "Al_2Cl_6", "C_6D_6 \\ (C_2H_5)_3N"'] & P_3N_3F_2\text{-}1,3\text{-}(C_6H_3D_2)_2\text{-}1,3\text{-}(C_6D_5)_2
\end{tikzcd}$$

Table I. Selected ^{1}H Nmr Parameters of Arylphosphazenes

Compd	Sol-vent	$J_{^{31}PH_o}$, Hz	δ_{H_o},[a] ppm	δ_{H_p},[a] ppm
$P_3N_3F_5C_6H_3D_2$	C_6D_6	16.0	−0.403	+0.170
	C_6H_{12}	16.5	−0.660	−0.330
1,1-$P_3N_3F_4(C_6H_3D_2)(C_6H_5)$	C_6D_6	13.0	−0.515	+0.175
	C_6F_6	14.0	−0.110	+0.130
cis-1,3-$P_3N_3F_4(C_6H_3D_2)_2$	C_6D_6	16.0	−0.630	+0.185
	C_6H_{12}	16.0	−0.650	−0.230
trans-1,3-$P_3N_3F_4(C_6H_3D_2)_2$[b]	C_6D_6	15.5	−0.550	+0.185
	C_6H_{12}	15.5	−0.550	−0.160
1,1,3,3-$P_3N_3F_2(C_6H_3D_2)_2(C_6D_5)_2$	C_6D_6	14.0	−0.800	+0.195
	C_6H_{12}	14.0	−0.580	−0.120

[a] Relative to C_6H_6. [b] Obtained on a mixture of cis and trans isomers after eliminating peaks due to the cis isomer.

are a function of both the electronic structure of the molecule and the diamagnetic anisotropic effect of the substituent, the para chemical shift is dependent only on the π-electron density at the para carbon atom.[15] The para proton shifts correlate well with the corresponding ^{13}C chemical shifts and the calculated charge densities at the para position.[15] The para proton chemical shift for $P_3N_3F_5C_6H_3D_2$ (in cyclohexane) is essentially equivalent to that of nitrobenzene under identical conditions.[15] Therefore, the phosphazene ring is a strongly electron-withdrawing substituent with respect to the benzene ring. Since para proton shifts are believed to reflect π-electron densities at the para carbon atom, this electron withdrawal is accomplished *via* a conjugative mechanism. The results for the phenyl-substituted cyclotriphosphazenes are in agreement with the corresponding studies on the fluorinated phenyl derivatives.[7]

The addition of more phenyl groups to the phosphazene ring results in increased shielding of the para proton and hence less conjugative interaction. This effect is fairly large (21 Hz from $P_3N_3F_5C_6H_3D_2$ to $P_3N_3F_2(C_6H_3D_2)_2(C_6D_5)_2$) and the question as to what role inductive effects have in this variation arises. The value of the ortho-meta proton coupling constant (J_{om}) remains at 7.5 ± 0.5 Hz through the series. Since J_{om} can be related to the substituent electronegativity in substituted benzenes,[16] it appears that changes of this type may not be crucial in determining changes in the para chemical shift. The observation of decreased phenyl-phosphorus conjugation with increased phenyl substitution is in contrast to the increase observed in fluorine atom back bonding through the same series.[11]

The cis and trans isomers of 1,3-$P_3N_3F_4(C_6H_3D_2)_2$ exhibit different chemical shifts (in cyclohexane) for both the ortho and the para protons. The difference between the ortho shifts is constant on going from cyclohexane to benzene-d_6 suggesting an intermolecular effect. Although axial-axial interactions may be important in dimethylaminochlorocyclotriphosphazenes,[17] an examination of models of the nongeminal diphenyl derivatives with the phosphazene in the chair conformation indicates that the ortho protons in the trans isomer would be deshielded *via* interaction with an axial fluorine atom. The opposite effect is observed. Since there are separate resonances for the para protons in the cis and trans isomers, the difference in the interactions probably lies in bonding differences. The observed shifts are in the direction predicted by the "cis effect;" *i.e.*, the phenyl group cis to a fluorine atom is labilized.[10] However, structural features of the system may also be involved. In a chair conformation, one phenyl group must be in an axial site for the trans isomer or the trans isomer may be in the boat conformation where both phenyl groups are in equatorial sites. There is some evidence for different nmr parameters for axial *vs.* equatorial sites in trimeric sulfanuric fluoride derivatives.[18]

Upon going from the supposedly noninteracting solvent cyclohexane to the basic solvent benzene-d_6, marked changes in the proton chemical shifts of the phenylcyclotriphosphazenes are observed. The para protons are considerably more shielded and exhibit only a barely detectable upfield shift with increasing phenyl content. The para protons on the other hand are considerably more deshielded and become progressively more deshielded with increasing degrees of substitution on the cyclotriphosphazene ring.

Benzene molecules tend to align themselves with the positive end of a dipole in solution.[19] One could envision a model in which the electron-deficient phenyl group and the benzene molecule stack in a parallel fashion with the para proton of the phenyl group under the center of the benzene molecule resulting in shielding of the para proton. The ring current of the solvent benzene would result in a deshielding of the ortho protons. One could also envision the para proton of the phenyl group pointed directly into the center of a benzene molecule which is perpendicular to the plane of the phenyl group. This latter model does not explain the deshielding of the ortho protons and neither model satisfactorily explains the large downfield shift of the ortho protons with increased degree of substitution of the cyclotriphosphazene ring.

Hexafluorobenzene has been shown to produce solvent shifts in which the protons at the positive end of a dipole are deshielded.[20] Although the para proton in 1,1-$P_3N_3F_4(C_6H_3D_2)(C_6D_5)$-hexafluorobenzene is deshielded with respect to the value in benzene-d_6 solution, it is still upfield from the value obtained in cyclohexane.

The magnitude of the phosphorus-ortho proton coupling

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constant, J_{PH_o}, is in the range observed in other arylphosphorus compounds.[14,21] It is interesting to note that, although the difference is small, J_{PH_o} is lower for a geminal configuration at the phosphorus center than for a nongeminal configuration. A similar situation is observed in the dimethylaminochlorocyclotriphosphazenes.[22] The origin of this difference could lie in the smaller bond angle (and hence less s character) expected in a $\equiv P(C_6H_5)_2$ center compared to a $\equiv PF(C_6H_5)$ center.[23] However, due to the proximity of the ortho proton to the phosphorus atom, orbital and dipolar contributions may be significant factors in determining the magnitude of J_{PH_o}. Similar effects have been postulated for the tin-ortho proton coupling constants in phenyltin trihalides.[24]

In conclusion, we have shown that examination of the proton nmr spectra of phenylcyclotriphosphazenes provides information concerning electronic interactions in these systems and could be a useful technique for establishing the presence and configuration of isomers in solution.

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Registry No. $P_3N_3F_5C_6H_3D_2$, 50859-00-2; 1,1-$P_3N_3F_4(C_6H_3D_2)(C_6H_5)$, 50859-01-3; *cis*-1,3-$P_3N_3F_4(C_6H_3D_2)_2$, 50859-02-4; *trans*-1,3-$P_3N_3F_4(C_6H_3D_2)_2$, 50859-03-5; $P_3N_3F_2$-1,3-$(C_6H_3D_2)_2$-1,3-$(C_6D_5)_2$, 50932-73-5.

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Studies of Sulfur Imides in Basic Organic Solvents. Synthesis and Characterization of Tetra-*n*-butylammonium Perthionitrate, $(n\text{-}C_4H_9)_4N(NS_4)$[1]

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Solutions of heptasulfur imide (S_7NH) in hexamethylphosphoramide (HMPA) are deep blue. The blue species has been isolated as the tetra-*n*-butylammonium salt and characterized as the NS_4^- anion. Infrared and Raman spectra suggest a branched chain structure. Solutions of S_7NH in dimethylformamide (DMF) contain both S_7N^- and NS_4^- in equilibrium; spectrometric and conductometric results were used to estimate the "aqueous" pK_a (S_7NH) at 25° to be about 5 and to calculate the equilibrium constant for the reaction $S_7N^- \rightleftharpoons NS_4^- + {}^3/_8S_8$, $K_i = 0.13 \pm 0.06$. Solutions of 1,4-$S_6(NH)_2$ in HMPA slowly turn blue to give 1 mol of NS_4^- per $S_6(NH)_2$.

Introduction

It has been known for many years that all the sulfur imides except tetrasulfur tetraimide give an intense blue coloration in basic organic solvents. This reaction is commonly used as a spot test in the chromatographic separation of the sulfur imides[2] and is dramatically apparent during their preparation from sulfur monochloride and ammonia in DMF. Lux and Anslinger suggested that the blue species formed by S_7NH in dimethyl sulfoxide (DMSO) was identical with that formed by alkali polysulfides in DMSO and erroneously attributed this color to neutral sulfur radicals, S_x (x = 2–4).[3] Chapman and Massey reported that the blue species from S_7NH in DMSO is negatively charged but exhibits no esr signal; they suggested it is the S_7N^- anion.[4] More recently Olsen and coworkers have carefully investigated the alkylation of sulfur imides under basic conditions. They were able to prove the existence of the S_7N^- anion in their blue tetrahydrofuran (THF) solutions but were unable to relate the color to any particular species.[5] The sodium salt, NaS_7N, which had previously been isolated,[6] is olive green. Finally, Mendelsohn and Jolly showed that in THF solution at −78° the S_7N^- anion is stable and yellow, but on warming above −40° it exists in equilibrium with the blue species which, therefore, is not *cyclo*-S_7N^-.[7]

We have reported that solutions of alkali polysulfides[8] or elemental sulfur[9] in HMPA are deep blue due to the presence of the S_3^- radical anion. We therefore decided to investigate the sulfur imides in HMPA, initially to determine if S_3^- is responsible for the color.

Experimental Section

Materials. HMPA (Aldrich) was dried with sodium hydride, stirred with sufficient potassium metal to turn the batch completely blue, vacuum distilled under nitrogen [bp 90° (4.7 mm); lit. bp 115° (15 mm) or 68° (1 mm)[10]], and then trickled through a column of freshly regenerated Linde 4A molecular sieves. DMF (Fisher) was degassed with a stream of nitrogen and then trickled through freshly regenerated Linde 4A molecular sieves. Purified solvents were stored and used in a dry oxygen-free atmosphere (Vacuum Atmospheres drybox). S_7NH was prepared from sulfur monochloride and am-

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