afforded $PhB(OCH_2CF_3)Cl$ (**3**) as a colorless liquid in 95% yield. The mixture of compounds (**2**, **4**, and **5**) was prepared in the same manner except that the BCl_3 ($^1/_2$ equiv) was condensed into a solution of $(CF_3CH_2O)_3B$ (**2**) in pentane at −78 °C. Distillation through a 10-cm column afforded a center fraction (bp 82–100 °C/760 mm) that was identified as the monochloroborane **4**.

Preparation of $Me_2NB(Ph)OCH_2CF_3$ (6). The phenylchloroborane **3** (6.5 g, 29 mmol) was combined with dry CH_2Cl_2 (ca. 30 mL) and cooled to 0 °C. Then Me_3SiNMe_2 (4.6 mL, 29 mmol) was slowly added via syringe, and the solution was allowed to warm to room temperature and was stirred overnight. Fractional distillation afforded **6** as a colorless liquid. In a few attempts of this reaction, an unidentified impurity (^1H NMR: δ 2.44) developed during distillation, which could not be removed by repeated distillations.

Preparation of $(Me_3Si)_2NB(Ph)OCH_2CF_3$ (7). A 250-mL, one-necked flask, was charged with $(Me_3Si)_2NH$ (6.3 mL, 30 mmol, 4.8 g) and dry Et_2O (30 mL). After cooling to 0 °C, *n*-BuLi (12 mL, 30 mmol, 2.5 M) was slowly added. The solution was allowed to warm to room temperature, stirred for 30 min, and then recooled to 0 °C. Compound **3** (6.7 g, 30 mmol) was added dropwise to the cold anion slurry. The mixture was stirred overnight, then filtered under nitrogen to remove LiCl. The solvents were removed under reduced pressure. Distillation afforded **7** as a colorless liquid.

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Complexes of Hexaphenoxycyclotriphosphazene and Sulfur Trioxide

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Introduction

Most of the known addition compounds[1-3] of cyclotriphosphazene, $(NPX_2)_3$, involve halogen (X = F, Cl, Br) and alkylamino (X = NHR, NR_2) substituted derivatives, as ligands, and the acceptor coordinated to the ring nitrogen. The aryloxy derivatives (X = OAr) have not been studied as much. On the basis of ^{31}P NMR spectroscopic data and relative basicity arguments, Horn and Kolkmann[4] concluded that hexaphenoxycyclotriphosphazene, $[P(OAr)_2{=}N]_3$ (II), yields an addition compound with BCl_3 and that the metal halide coordinates to the endocyclic nitrogen of the phosphazene rather than to the exocyclic oxygen. On the other hand, alkylation studies of substituted cyclotriphosphazenes[5] suggest that the phenoxy substituents reduce (or mask), by steric effects, the basicity of the endocyclic nitrogen and, thus, favor the reaction at the pendent substituent. Finally, in the sulfonation of the linear polymer[6] $[-NP(OAr)_2-]_{15000}$ (I), the electrophilic attack of N by SO_3 is probably the first reaction step:

$$-P(OAr)_2{=}N- + SO_3 \rightarrow -P(OAr)_2{=}N{\cdot}(SO_3)- \quad (1)$$

Using II to mimic[7] the reactivity of the high polymer I, we expected in this spectroscopic study to find direct evidence of the favored coordination site in the $-NP(OAr)_2-$ moiety.

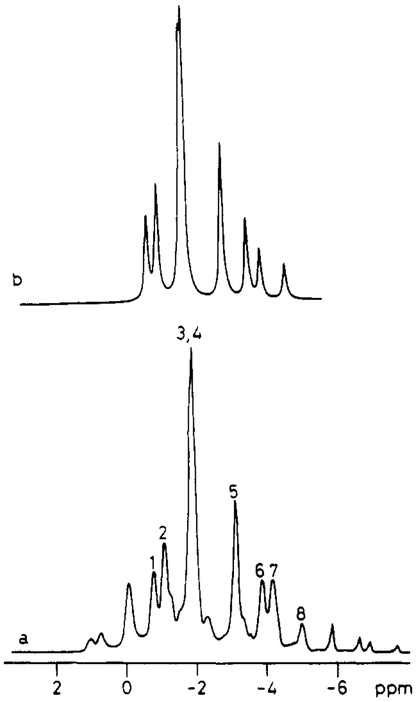

Figure 1. Simulated (b) and experimental (a) ^1H-decoupled ^{31}P NMR spectra of complex V (SO_3/II mole ratio = 3.0) recorded in CH_2Cl_2 at 80.961 MHz and at −90 °C. Signals 1–8 identify the resonance pattern coincident with the simulated spectra. Other signals are discussed in text.

Experimental Section

Sulfur trioxide[8] and II[9] were obtained as previously reported. All other reagents are C. Erba RPE products.

II (1 g) was dissolved in 5 mL of a chlorinated solvent (*sym*-dichloroethane, $CDCl_3$, $CHCl_3$, CH_2Cl_2 or CD_2Cl_2) at $-30 \geq T$ (°C) ≤ 0, and SO_3 was added [$0.5 \leq SO_3$/II (mol/mol) ≤ 3.0] under N_2 and stirring. The system was then kept at room temperature for 3 h and filtered to separate some deposited solid material (≤5 wt % initial II). The solid, washed with fresh solvent and dried under vacuum, was found to be soluble in water and to contain organic sulfur by total sulfur-inorganic sulfur analysis.[8a] The filtrate was analyzed by IR and NMR spectroscopy, as such and after addition of 1,4-dioxane. Duplicate mixtures were made at each mole ratio as above, and 30 mL of water was added at the end of the reaction time. The aqueous phase was separated from the organic layer and then extracted twice with equal volumes of the fresh organic solvent. Evaporation of the combined organic extracts to dryness left a residue (95–98 wt % initial II). This residue was identified as II by its IR and NMR spectra, which were identical with those of an authentic sample.

The IR spectra (AgCl plates; liquid films) were recorded under nitrogen by using a Perkin-Elmer 782 spectrometer. ^1H NMR spectra were recorded on a WP-80 Bruker spectrometer operating in the Fourier transform mode at 80 MHz. The ^{13}C and ^{31}P NMR spectra were recorded by using a Varian XL-200 spectrometer at 50.288 and 80.961 MHz, respectively. ^1H and ^{13}C chemical shifts [$\delta(^1H)$ and $\delta(^{13}C)$, ppm] are referred to internal TMS. ^{31}P chemical shifts [$\delta(^{31}P)$, ppm] are

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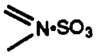
referred to external 85% H_3PO_4. Integration of the experimental resonance signals (Figure 1a) assigned to P_1 and P_3 (signals 1–4) and of the signals assigned to P_2 (signals 5–8) yields a 2/1 elemental ratio, as expected for the A_2B spin system, which is discussed below.

Results and Discussion

Chemical and Spectroscopic Evidence of Donor–Acceptor Interactions in the Solutions of II and SO_3. SO_3[10] is a strong electrophile that yields donor–acceptor addition compounds with molecules containing -O- (i.e. dioxane) or =N- (i.e. pyridine) atoms. It yields covalent compounds, by H substitution, with aromatic rings. II contains all these nucleophilic sites: i.e. the endocyclic nitrogen, the exocyclic oxygen and the pendent aromatic ring. We found that, when SO_3 reacts with II at a SO_3/II mole ratio of ≤3.0, a limited amount of C-sulfonated product (≤5% relative to II) forms and that this product is easily separated from the reaction medium by filtration. This lack of reactivity at the aromatic carbons has also been found in the reaction of SO_3 with the linear polymer I[6] (at a SO_3/-P=N- mole ratio of ≤1.0) and with pyridine,[11] due to the formation of



addition compounds. On the contrary, with molecules not containing N atoms as donor sites,[8,12] the electrophilic substitution of a C–H hydrogen by SO_3 occurs with higher yields.

In this work, evidence of a donor–acceptor interaction in solution between II and SO^3

$$\mathrm{II} + n\mathrm{SO_3} \rightleftharpoons \mathrm{II}\cdot n\mathrm{SO_3} \qquad (2)$$

has been obtained. SO_3 was added to the solution of II in $CDCl_3$ at a SO_3/II mole ratio of 3/1. The IR spectrum of the solution, after filtration of the minor amount of insoluble C-sulfonated product, showed that the bands of unreacted SO_3 were missing, that a new band at 1315 cm^{-1} was present, and that the main bands of neat II (ν = 950 and 1010 cm^{-1}) were shifted to 990 and 1020 cm^{-1} and altered in shape. Similar changes between the spectra of the separate reagents and of the reagent mixture were observed by using $CHCl_3$, CH_2Cl_2, or CH_2ClCH_2Cl as solvent. Also, the ambient probe temperature proton-decupled ^{31}P NMR spectra of these mixtures showed one ^{31}P resonance signal that was shifted ca. 10–12 ppm downfield from that recorded for neat II (δ = 9.54 ppm in $CDCl_3$ and δ = 8.72 ppm in CD_2Cl_2 for II; δ = -0.02 ppm in $CDCl_3$ and δ = -2.64 ppm in CH_2Cl_2 for II and SO_3 at a reagent mole ratio of 3.0). These changes were reversible upon further manipulation of the reagent mixtures. By addition of 1,4-dioxane (in 2 mol excess over the initial SO_3) the phosphazene IR bands reverted to the frequencies and shapes as in neat II, and the band at 1315 cm^{-1} disappeared. The ^{31}P NMR spectral signal shifted back to the value for neat II. Furthermore, addition of water to the reagent mixtures allowed recovery of almost all initial II. Vacuum evaporation of the reagent mixtures, following the addition of SO_3, left a solid residue whose IR spectrum was similar to that of II.

Our results demonstrate that an interaction between SO_3 and II does occur and that this must involve labile donor–acceptor bonds as in the complex II·nSO_3: SO_3 may thus be displaced from the complex as follows: by addition of water and formation of sulfuric acid

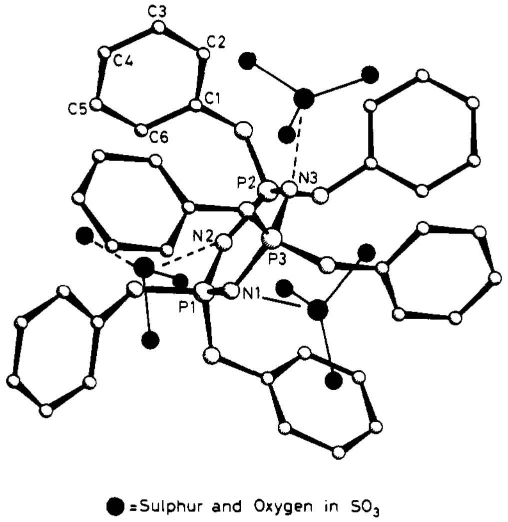
$$\mathrm{II}\cdot n\mathrm{SO_3} + n\mathrm{H_2O} \rightarrow \mathrm{II} + n\mathrm{H_2SO_4} \qquad (3)$$

by a competing donor (D = dioxane)

$$\mathrm{II}\cdot n\mathrm{SO_3} + m\mathrm{D} \rightarrow \mathrm{II} + m\mathrm{D}\cdot n\mathrm{SO_3} \qquad (4)$$

or by vacuum evaporation and shifting of equilibrium 2 to the left. This last behavior has been previously observed for the complexes of hexachlorocyclotriphosphazene and SO_3.[13]

Detection of the Complex II·3SO_3 (V) in Solution. In the IR spectra of the II–SO_3 mixtures, the bands due to free SO_3[14] were absent across the 0.5–3.0 reagent mole ratio (SO_3/II) range, indicating that most SO_3 is complexed by the phosphazene. According to eq 2, this result can be obtained at a mole ratio of 3.0 only if V is largely the dominant species in the system.



V

Calculations based on the concentration of the initial SO_3 in the mole ratio = 3.0 solution (i.e. 4.7 wt %) and on the lowest detectable concentration of free SO_3 in the IR sample (ca. 0.4 wt %) indicate that the yield of V, relative to initial II, is greater than 90 mol %.

Coordination of SO_3 at the nitrogen in II is deduced on the basis of the above reported change of the ^{31}P resonance and on no change observed in the ambient probe temperature ^1H and ^{13}C NMR spectra, upon passing from neat II to the II/SO_3 mole ratio = 3.0 solution. Vice versa, complexation at the exocyclic oxygen in the phosphazene should have also affected the resonances of the aromatic carbons, similar to the case of the complexes[15] of phenyl ethers and boron halides.

Additional structural information of V was obtained at low temperature. The ^{31}P NMR spectrum of the mole ratio = 3.0 solution in CH_2Cl_2 at -90 °C (Figure 1a) exhibits a well-resolved A_2B multiplet. The same multiplet was recorded in $CDCl_3$ at -50 °C. The refined parameters produced for the spectrum (Figure 1b) calculated by means of the Bruker PANIC 81 computer program were $\delta(P_1) = \delta(P_2) = -1.48$ ppm, $\delta(P_3) = -3.84$ ppm, $J(P_1,P_3)$ = 0 Hz, and $J(P_1,P_2) = J(P_2,P_3)$ = 81.2 Hz. Nonequivalent phosphorus nuclei in V could arise because one SO_3 is bonded differently from the other two, due to steric crowding around the rigid P=N cycle. For free II, our dipole moment studies[16] in solution have shown that the molecule lies more favorably in a number of structures involving the asymmetric arrangement of the phenoxy rings about the P=N cycle. However, the ^{31}P spectra of II in solution showed a singlet, even at low temperature (δ = 10.08 ppm, $w_{1/2}$ = 8.52 Hz in $CDCl_3$ at -50 °C; δ = 9.46 ppm, $w_{1/2}$ = 11.35 Hz at -90 °C in CD_2Cl_2), probably due to fast interconversion between conformations. Analogously, nonequivalent aromatic rings in a 2/1 ratio were observed at -90 °C for V and not for II. Indeed, the ^1H-decoupled ^{13}C NMR

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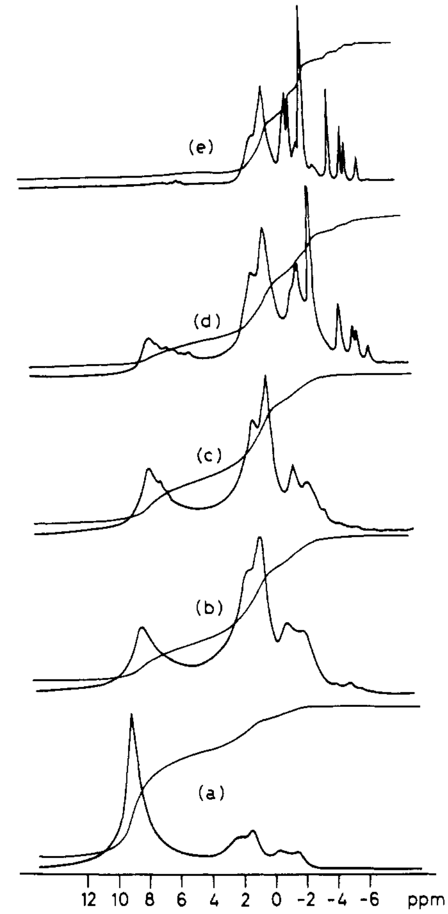

Figure 2. 80.961-MHz ^{1}H-decoupled ^{31}P NMR spectra of the solutions of II and SO_3 in CH_2Cl_2 at -90 °C. Mole ratio: 0.5 (a); 1.0 (b); 1.5 (c); 2.0 (d); 2.5 (e).

spectrum of the mole ratio = 3.0 solution in CH_2Cl_2 contained sharp singlets at room temperature (δ = 122.2 for C_2 and C_6, 128.4 for C_4, 131.9 for C_3 and C_5, and 150.5 ppm for C_1),[6] each signal splitting at -90 °C into a doublet with a 2/1 area ratio. By comparison, for neat II, no splitting of signals occurred upon lowering the temperature to -90 °C.

The ^{31}P spectrum Figure 1a also contains low-intensity signals at $\delta < -5.5$ ppm and at $\delta > 0$ ppm, revealing the presence of other minor A_2B spectral features and, therefore, of one and maybe two lesser (<15 mol %) isomers or conformational isomers of V. These signals were absent in the $CDCl_3$ spectrum.

The Complexes II·SO$_3$ (III) and II·2SO$_3$ (IV). At mole ratio (R) = 0.5–2.5 and at ambient probe temperature, a single ^{31}P resonance signal was obtained: for R = 1.0, δ = 1.56 ppm in CH_2Cl_2 and δ = 6.89 ppm in $CDCl_3$; for R = 2.0, δ = -1.75 ppm in CH_2Cl_2 and δ = 0.34 ppm in $CDCl_3$. At -90 °C the ^{31}P NMR spectra of the same mixtures in CH_2Cl_2 (Figure 2) showed poorly resolved signals. At -50 °C in $CDCl_3$, resolution was still worse.

The formation of III and IV at $R < 3.0$ is readily envisioned from eq 2. Similar to V, these complexes may lie in a number of conformations as a result of intramolecular interconversion processes. Faster intermolecular exchange of SO_3 molecules, leading to the presence of species having different chemical composition, is also possible in this case

$$2\mathrm{III} \rightleftharpoons \mathrm{IV} + \mathrm{I} \qquad (5)$$

$$2\mathrm{IV} \rightleftharpoons \mathrm{III} + \mathrm{V} \qquad (6)$$

Indeed, Figure 2 shows the presence of free II (δ = 9.46 ppm in Figure 2 as well as in the spectrum of the authentic compound) up to R = 2.0 and of V ($\delta < 0$) already at R = 2.0. The remaining signals, whose maximum intensity is reached for samples at R = 1.0 ($\delta \simeq$ 1.0 ppm) and at R = 1.5 ($\delta \simeq$ 0.2 ppm), are likely to be associated with the monocoordinated and dicoordinated compounds III and IV, respectively, on the basis of the order of appearance with increasing R and the order of decreasing δ as the number of complexed donor sites in the molecule increases. Equations 5 and 6 make the observation of free II up to R = 2.0 consistent with the absence of free SO_3 as indicated by IR spectroscopy. Under these circumstances, III and IV cannot be characterized as well as V.

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Registry No. II, 1184-10-7; III, 130551-85-8; IV, 130551-86-9; V, 130551-84-7; SO_3, 7446-11-9.