PF_3 and OPF_3 suggesting that each F_{1s} component in PF_5 arises from a chemically distinct fluorine type.[16] The two components are reasonably assigned to equatorial and axial fluorine atoms in keeping with the established trigonal-bipyramidal molecular structure of PF_5.[17] That the greater component (3 units) which arises from the equatorial fluorine atoms lies to higher binding energy of the lesser intensity (2) component due to the axial fluorine atoms is consistent with the shorter P–F bond distance (and therefore stronger binding) in the equatorial plane. Recent calculations[18] on PF_5 and related molecules confirm the expectation of stronger and shorter equatorial bonds.

Experimental Section

Any physical study of reactive fluorides requires extensive precautions to ensure that hydrolysis of the compound does not occur. The present measurements were done with commercial samples of PF_3, OPF_3, and PF_5 each having a purity greater than 98% (as determined by infrared spectroscopy). The gases were introduced into the gas sample cell of the Berkeley iron-free spectrometer[19] through stainless steel tubing which had been baked (200°C) under vacuum and then repeatedly flushed with the fluorides in order to remove all traces of moisture before establishing the sample flow. The chlorides were also commercial materials and were introduced as gases into the supply lines which had been previously exposed to the fluorides and so were probably free of traces of moisture. The spectra were measured at pressures of the order of 5×10^{-2} Torr and were calibrated by introducing, simultaneously with the compound, an approximately equal pressure of gaseous Ar ($2p_{3/2}$ = 248.62 eV)[20] with known binding energy. Line widths given as fwhm in Table I were determined on data obtained in the absence of calibrant. The raw data, obtained on a momentum base, were converted to a linear kinetic energy scale and the corrected data were fitted to a gaussian line shape by an iterative nonlinear least-squares curve-fitting program.[4] Additional support for the validity of the PF_5 F_{1s} data is provided by the reproducibility of the asymmetric line shape over several determinations on different occasions suggesting that impurity or decomposition is not responsible for the two-component F_{1s} line. Furthermore the F_{1s} spectrum did not change with time and, finally, monitoring the O_{1s} region during accumulation of F_{1s} data for PF_5 showed that no significant concentration of OPF_3 was present. Line shapes for F_{1s} of OPF_3 and PF_3 were symmetric which supports the proposal of two F_{1s} components in PF_5.

Data for SPF_3 and some of the other compounds mentioned herein were obtained on a McPherson ESCA-36 photoelectron spectrometer using precautions similar to those described above to prevent hydrolysis in the sample-handling system. The data, obtained in this case on a linear kinetic energy scale, were analyzed in a fashion similar to that above, using a modified version of the same least-squares fitting program.[4]

Acknowledgment. I am indebted to Drs. J. M. Hollander and D. A. Shirley of the Lawrence Berkeley Laboratory for the use of facilities and for their generous hospitality, to Drs. Neil Bartlett and C. J. Adams for assistance with the infrared measurements, and to the University of Alberta for generous sabbatical leave and financial support. This work was supported in part by the U.S. Atomic Energy Commission.

Registry No. PF_3, 7783-55-3; OPF_3, 13478-20-1; SPF_3, 2404-52-6; PF_5, 7647-19-0; PCl_3, 7719-12-2; $OPCl_3$, 10025-87-3; $SPCl_3$, 3982-91-0; P, 7723-14-0; F, 7782-41-4; O, 7782-44-7; Cl, 7782-50-5; S, 7704-34-9.

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Mechanism of the Reactions between Ortho Dinucleophiles and Cyclophosphazenes[1,2]

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Phosphoranes are formed when halocyclophosphazenes or spiro[arylenedioxycyclophosphazenes] react with ortho dinucleophiles such as catechol and base or *o*-aminophenol. With the latter reagent, a critical intermediate in the degradation pathway, iminobis[spiro[bis(*o*-phenyleneoxyamino)phosphorane]], has been isolated. The effects of temperature, solvent, and other nucleophiles on these reactions have been analyzed, and the reaction pathways are discussed.

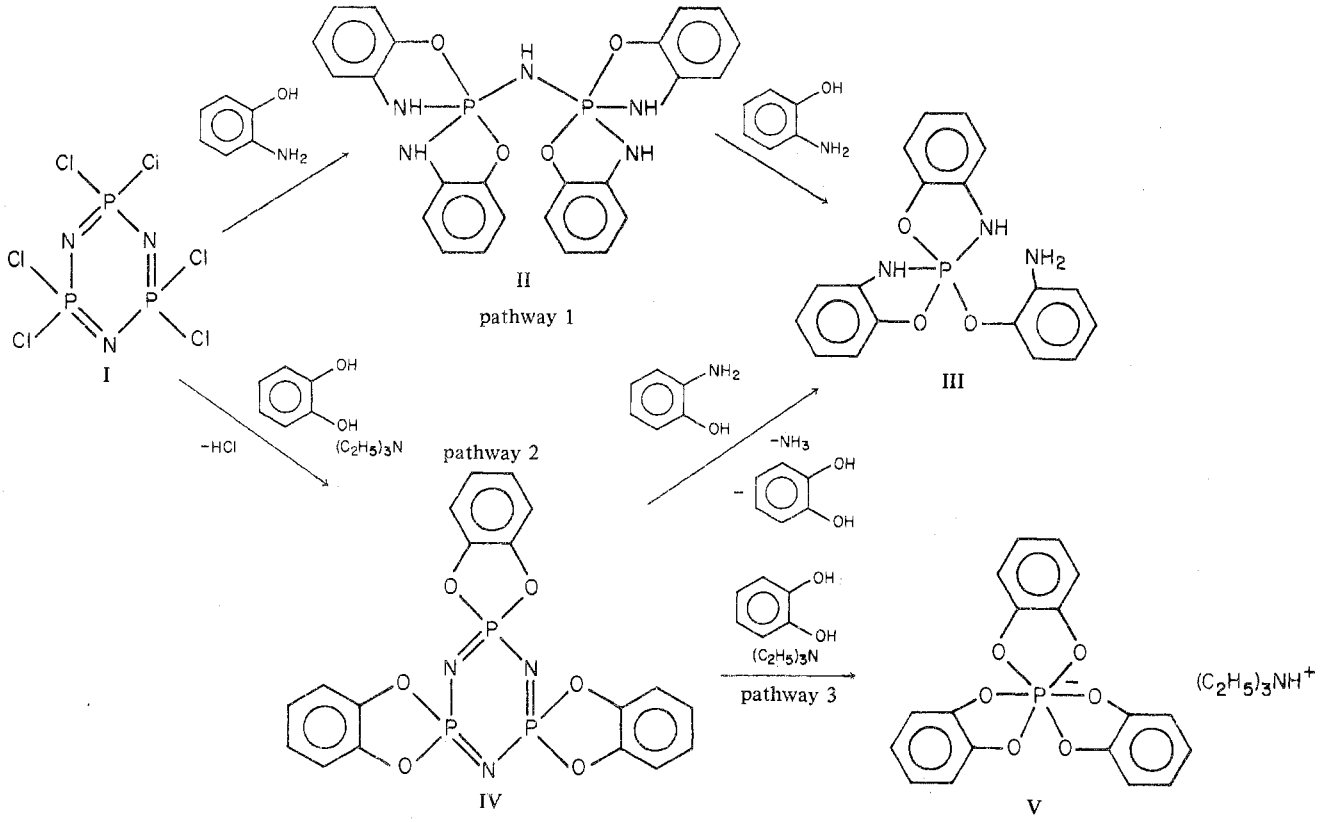
Introduction

Cyclic and polymeric halophosphazenes undergo a broad range of nucleophilic substitution reactions with alkoxides, aryl oxides, or amines to generate organophosphazenes by processes such as eq 1. Approximately 650 cyclic organophosphazenes (n = 3 or 4) have been synthesized by this route, together with more than 60 high molecular weight polymers ($n \approx 15{,}000$). The high polymers, in particular, show considerable promise

$$(NPCl_2)_n \xrightarrow[-NaCl]{NaOR} [NP(OR)_2]_n \qquad (NPCl_2)_n \xrightarrow[-HCl]{RNH_2} [NP(NHR)_2]_n \qquad (1)$$

for technological applications. In all of these reactions the phosphazene backbone is essentially unaffected by the halogen replacement process. However, as an outgrowth of our studies

Scheme I



on such reactions, it was found that ortho-substituted aromatic dinucleophiles behave differently. Such reagents show a marked tendency to induce cleavage of the phosphazene skeleton.

Halocyclophosphazenes (I) or spiro[arylenedioxycyclophosphazenes] (such as IV) react with *o*-aminophenol or with catechol and base to yield phosphoranes by a phosphazene ring degradation process.[3,4] These reactions are illustrated in Scheme I and are typified by the conversion of hexachlorocyclotriphosphazene (I) to spiro[bis(*o*-phenyleneoxyamino)-2-aminophenoxyphosphorane] (III) or to the tris(*o*-phenylenedioxy)phosphate ion (V). The driving force for these reactions appears to be the release of exocyclic ring strain associated with the conversion of spirocyclic phosphazenes (such as IV or the analogous unstable tris(*o*-phenyleneoxyamino)cyclotriphosphazene) to a spiro[phosphorane] or spiro[phosphate].[3,4] However, the details of the reaction pathways had not been determined. In this paper we examine the mechanisms of these reactions. Pathway 1 (Scheme I) will be considered first. Pathways 2 and 3 will then be discussed.

Results and Discussion

Pathway 1: Isolation and Characterization of Intermediate, II. In an earlier paper[4] we reported that hexachlorocyclotriphosphazene (I) or other halocyclo- or polyphosphazenes react with *o*-aminophenol in boiling xylene to yield a spiro[phosphorane] (III). It has now been shown that hexachlorocyclotriphosphazene reacts with *o*-aminophenol in xylene at temperatures between 100 and 138° to yield ammonium chloride, spiro[phosphorane] III, and an intermediate, iminobis[spiro[bis(*o*-phenyleneoxyamino)phosphorane]] (II). Compound II (mp 195–198°) can be separated from III by recrystallization, and the formation of II and III can be monitored by thin-layer chromatography techniques.

The infrared spectrum of II (Nujol mull) showed evidence for the groupings NH (3400 cm^{-1}), aromatic units (1610, 1493, and 770–710 cm^{-1}), P–O–aryl or P–N–aryl (1254, 1232, 810 cm^{-1}), and P–N (910 cm^{-1}). Mass spectra showed a parent peak at m/e 505 (the molecular weight of II is 505), and the base peak at m/e 243 and fragmentation peaks at m/e 397, 259, 312, and 138 were fully consistent with structure II. Microanalysis data (see Experimental Section) confirmed the composition.

Table I. Products from the Reaction of *o*-Aminophenol with Hexachlorocyclotriphosphazene (9:1 Molar Ratio) in Xylene[a]

Temp, °C	*o*-Aminophenol hydrochloride[b]	III[b]	II[b]
100	0	0	0.5
110	10.0	0.3	1.5
120	12.5	3.2	1.7
130	10.3	6.1	*c*
138	9.6	5.6	0.8

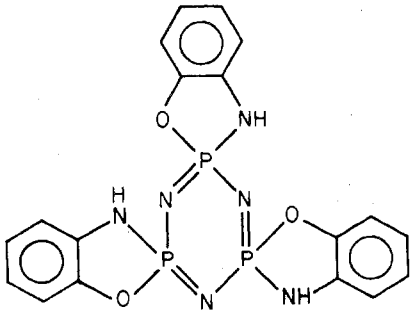
[a] Concentrations: *o*-aminophenol, 30×10^{-3} *M*; hexachlorocyclotriphosphazene, 3.3×10^{-3} *M*. [b] mmol $\times 10^3$. [c] Identified by thin-layer chromatography but not isolated.

The effect of temperature on the relative yields of II and III in xylene solution was examined over the temperature range 25–138°. In each case the molar ratio of *o*-aminophenol to I was 9:1. This allowed three molecules of *o*-aminophenol to react with I and six molecules of *o*-aminophenol to function as hydrohalide acceptor. Below 100° the reactions were heterogeneous and neither II nor III was detected in the mixture. As shown in Table I, at 100° II was detected but III was not found. At higher temperatures the yield of II remained constant or declined as the yield of III increased. This suggests that II is a direct intermediate formed during the conversion of I to III. Further evidence in favor of this view was provided by the fact that pure II reacted with *o*-aminophenol in boiling xylene to yield III.

Solvent effects are quite marked for the conversion of I to III in the presence of *o*-aminophenol. The formation of both II and III was accelerated as the solvent was changed in the sequence xylene < dibutyl ether < anisole < ethyl acetate <

dioxane < nitrobenzene < acetonitrile at 80°. With the exception of dioxane, this order parallels an increase in the dielectric constant of the solvents. The solvent changes did not appear to alter the products formed in the reaction mixture. The anomalous position of dioxane in this series may be a consequence of its complexing ability. However, the general influence of dielectric constant on the reaction is consistent with an ionic mechanism and it may reflect the rate of an initial attack by *o*-aminophenol on a phosphorus atom in hexachlorocyclotriphosphazene, perhaps facilitated by chloride ionization from phosphorus.

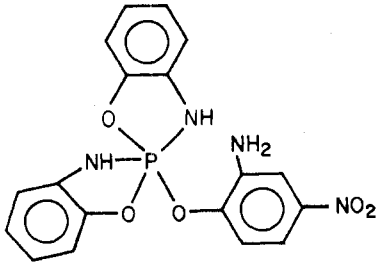
Pathway 1: Reaction Mechanism. The identification of intermediate II provides an important clue to the mechanism of this degradation reaction. It reinforces the view that the primary step in pathway 1 involves the formation of an unstable spiro[cyclophosphazene] such as VI, which reacts



VI

rapidly with *o*-aminophenol to yield II and ammonia. Presumably, the presence of the five-membered exocyclic rings in VI destabilizes the molecule to further nucleophilic attack. Indeed, the transformation of VI to II would provide a facile mechanism for the release of steric strain, since the trigonal-bipyramidal geometry at phosphorus in II provides an unstrained NH–P–O angle. This driving force would be absent in the conversion of II to III and this provides an explanation for the relative slowness of this step.

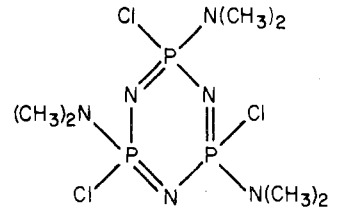
It is believed that the conversion of II to III requires the presence of free *o*-aminophenol in the reaction medium rather than an internal rearrangement of II. Evidence for this requirement was provided by the isolation of phosphorane VII



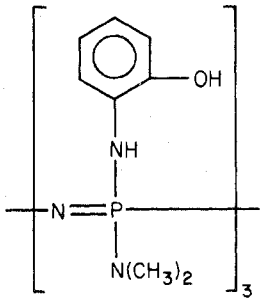
VII

from the interaction of II with 4-nitro-2-aminophenol.[7,8] Mixed-substituent phosphoranes were not isolated when phosphorane III was treated with 4-nitro-2-aminophenol, *o*-phenylenediamine, or catechol, although small amounts of *o*-aminophenol were released. Thus, it appears unlikely that the second ligand is scrambled into the system *after* conversion of II to III.

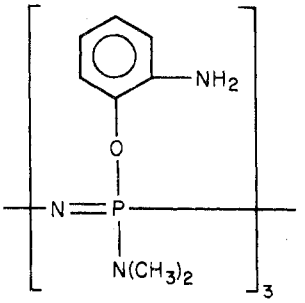
The reaction of I with *o*-aminophenol does not provide the most efficient route for the synthesis of II. A more effective procedure involves the reaction of 1,3,5-tris(dimethylamino)-1,3,5-trichlorocyclotriphosphazene (VIII) with *o*-aminophenol in boiling xylene (see Experimental Section). This displacement of dimethylamino groups from VIII by *o*-aminophenol is perhaps surprising when compared with the reactions of VIII with monoamines, monoalkoxides, or



VIII



IXa



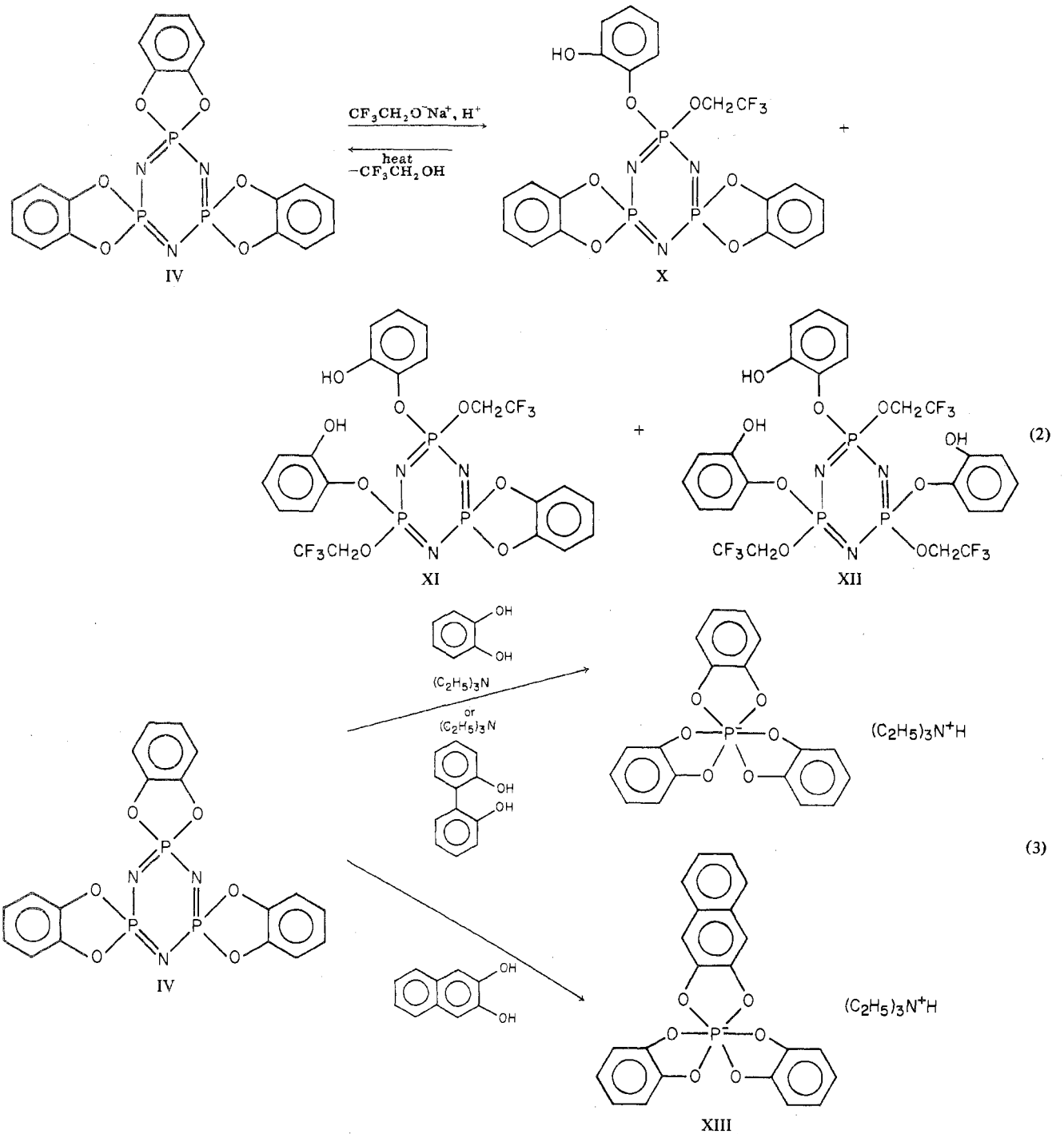
IXb

mono(aryl oxides), where only the chloro groups are displaced.[5] However, it is assumed that VIII reacts with *o*-aminophenol to yield IXa or IXb or their hydrochloride salts, which cyclize to VI with elimination of dimethylamine. Subsequent steps would then follow pathway 1. Compound IXb would appear to be a plausible intermediate if *o*-aminophenol reacts as its zwitterionic form, $o\text{-}N^{+}H_3C_6H_4O^{-}$.

Pathways 2 and 3. Pathways 1–3 apparently follow closely related mechanisms. However, since spiro[cyclophosphazene] VI could not be isolated from pathway 1, it was especially important to obtain mechanistic clues about the conversion of IV to phosphoranes. The following data were obtained with this in mind.

Specific mononucleophiles can cleave one or more of the exocyclic bonds in IV without inducing degradation to phosphoranes. For example, IV reacts with trifluoroethoxide ion to yield mono-, bis-, and tris(trifluoroethoxy) derivatives (X–XII), without loss of catechol (eq 2). Heating of these derivatives re-formed IV with loss of trifluoroethanol, and this provided evidence that the trifluoroethoxide substitution pattern was nongeminal. Phenol, *n*-propylamine, or piperidine reacted similarly with IV to yield products analogous to X–XII, and these products also regenerated IV when heated or stored. Equally revealing was the fact that phenol, *p*-nitrophenol, ethanol, or 2,2'-dihydroxybiphenyl in the presence of triethylamine induced the degradation of IV to V. No evidence was found that the mononucleophiles or 2,2'-dioxybiphenylene units became incorporated into the phosphorane product.

Several of the degradation reactions reported earlier[3,4] resulted in the complete displacement of one exocyclic unit at phosphorus in the cyclophosphazene by another cyclic unit during formation of the phosphorane (for example in the conversion of IV to III). Scrambling of the *cyclized* ligands must, therefore, occur at some stage in the degradation, and the prospect existed that spiro[phosphoranes] or spiro[phosphates] with mixed spiro units might be accessible. Tris(*o*-phenylenedioxy)cyclotriphosphazene (IV) was, therefore, treated with triethylamine and 2,3-dihydroxynaphthalene (see eq 3). The reaction conditions were similar to those used for the degradation of IV to spiro[phosphate] V.[3,6] Spiro[phosphate] XIII was isolated. This contained two *o*-phenylenedioxy units and one naphthalenedioxy unit in the molecule. However, when IV was allowed to react with 2,2'-dihydroxybiphenyl and triethylamine, degradation to V occurred without incorporation of the biphenylenedioxy units into the spiro[phosphate]. This further demonstrates the requirement that only five-membered ring systems are



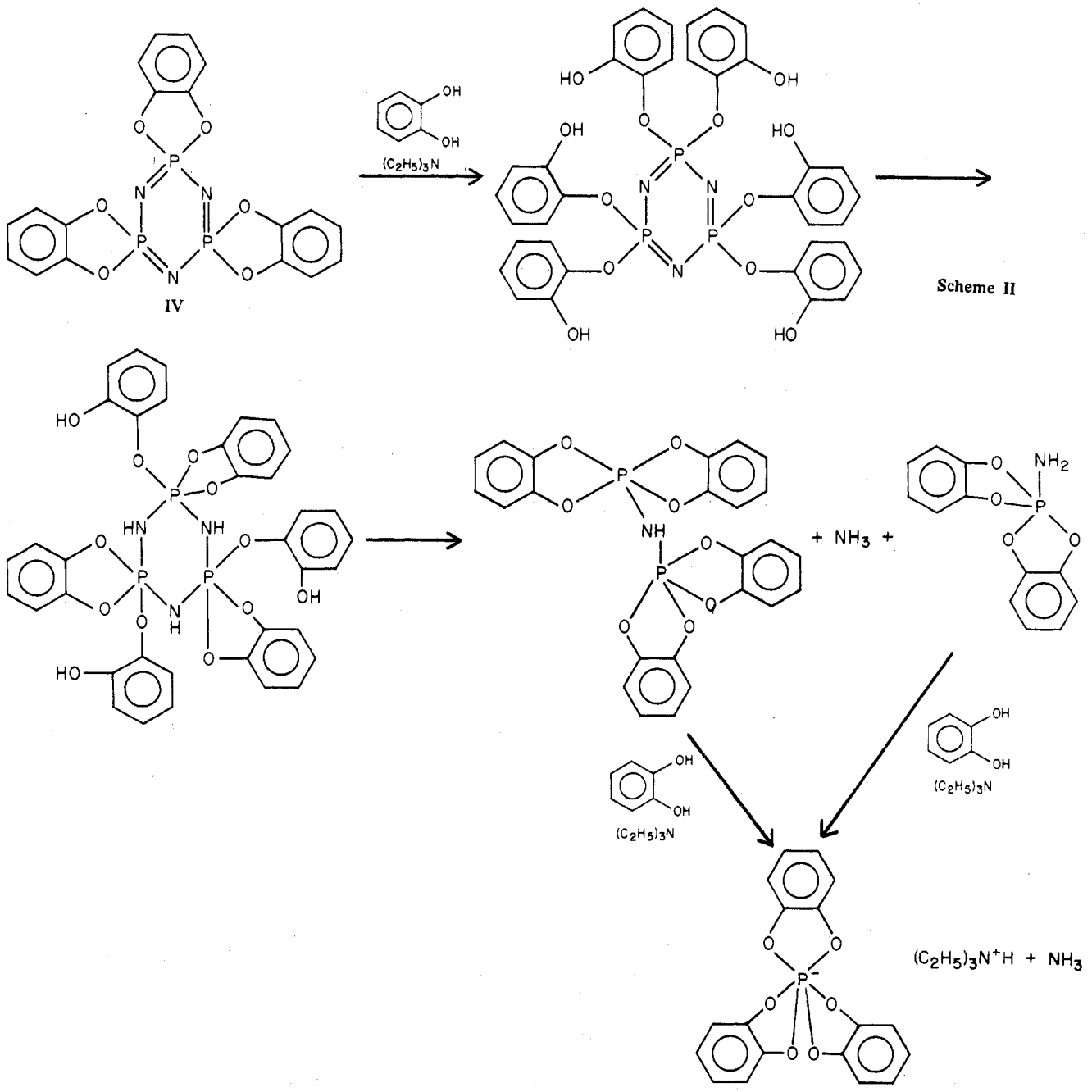
scrambled into the phosphorane or spiro[phosphate].

Related to this problem is the question of how three arylenedioxy or aryleneoxyamino units initially present on three separate phosphorus atoms are transferred to one phosphorus atom in the spiro[phosphate] or spiro[phosphorane]. This question is especially important for the degradations which occur in the presence of triethylamine plus phenol, *p*-nitrophenol, or 2,2'-dihydroxybiphenyl. A transannular, catechol-bridging mechanism appears unlikely, and the only acceptable alternative would require the presence of *free* catechol in the reaction medium. It is presumed that free catechol is liberated by the reaction of a mononucleophile with IV. The reaction sequence shown in Scheme II could then occur.

Finally, it is worthwhile to note that VIII reacts with catechol, in the *absence* of added base, to yield IV. However, if triethylamine is also present in the reaction mixture, V is isolated rather than IV. The same degradation of VIII to V occurs when VIII is treated with catechol and diethylamine hydrochloride. Hence, triethylamine is not a unique base in this reaction. However, spiro[cyclophosphazene] IV does not degrade to V in the presence of triethylamine hydrochloride when catechol is absent. Moreover, no degradation takes place if IV is treated with catechol in the absence of base. Thus, the suspicion exists that cleavage of the phosphazene skeleton requires the presence of an aryl oxide ion and that the triethylammonium ion alone is ineffective for this degradation.

Experimental Section

Synthesis of Iminobis[spiro[bis(*o*-phenyleneoxyamino)phosphorane]] (II). (a) From 1,3,5-Tris(dimethylamino)-1,3,5-trichlorocyclotriphosphazene (VIII). *o*-Aminophenol (6.45 g, 0.06 mol) and VIII (3.73 g, 0.01 mol) were allowed to react in boiling xylene (100 ml)



Scheme II

for 8 hr. After cooling, the solid formed was filtered off and xylene was removed from the filtrate on a rotary evaporator, to leave an orange-brown solid (3.5 g). This was washed with boiling toluene (100 ml) and the insoluble portion was dissolved in a minimum of tetrahydrofuran (11 ml). This was then diluted with *n*-heptane (210 ml). After several days crystals had formed. These were found to be II (0.4 g, mp 194–198°).

The solid obtained initially from the reaction mixture was washed with water. By thin-layer chromatography, the residue (5.5 g) was found to be a mixture of III and II.

(b) From Hexachlorocyclotriphosphazene (I). A solution of I (14.0 g, 0.04 mol) and *o*-aminophenol (26.3 g, 0.24 mol) in anisole (450 ml) was heated at reflux. Within 15 min a solid had precipitated from solution, but heating was continued for 18 hr. The mixture was filtered hot and petroleum ether (600 ml) was added to the cooled filtrate. This caused another precipitate to form. This was filtered off and the solvent was evaporated from the filtrate to leave a brown solid. Recrystallization from *n*-heptane gave II (0.7 g, mp 195–198°). Anal. Calcd: C, 57.1; H, 4.16; N, 13.86; P, 12.28. Found: C, 56.85; H, 4.55; N, 13.75; P, 12.35.

Reaction of *o*-Aminophenol with Hexachlorocyclotriphosphazene (I). Effect of Temperature Variations. Reactions were performed at 25, 50, 75, 100, 110, 120, 130, and 138° in xylene solution. The following example illustrates a typical procedure. *o*-Aminophenol (3.27 g, 0.03 mol) was added to a stirred solution of I (1.16 g, 0.0033 mol) in xylene (100 ml) maintained at 110° in a nitrogen atmosphere. After 18 hr of reaction the mixture consisted of an orange solution, a fine, pale solid, and a cluster of large crystals. The crystals were identified by infrared spectra as *o*-aminophenol (0.9 g), and the finely divided solid was *o*-aminophenol hydrochloride (1.44 g) identified on the basis of infrared comparisons. Cooling of the orange solution yielded additional quantities of *o*-aminophenol (0.77 g), which was removed by filtration. Solvent was removed from the filtrate and the residue was extracted with petroleum ether to yield a brown solid (0.88 g). This was extracted with benzene to leave a residue of spiro-[bis(*o*-phenyleneoxyamino)-2-aminophenoxyphosphorane] (III) (0.12 g), identified by its infrared spectrum. Benzene was evaporated from the extract to yield iminobis[spiro[bis(*o*-phenyleneoxyamino)-phosphorane]] (II) (0.76 g), identified by its infrared spectrum and thin-layer chromatographic retention. Solvent was removed from the petroleum ether extract to yield unreacted hexachlorocyclotriphosphazene (I) (0.61 g).

Solvent Changes in the Reaction of Hexachlorocyclotriphosphazene (I) with *o*-Aminophenol. The general experimental procedure involved the reaction of I (1.16 g, 0.0033 mol) with *o*-aminophenol (3.27 g, 0.03 mol) in the chosen medium (100 ml) at 80° under an atmosphere of dry nitrogen. The presence and relative concentrations of *o*-aminophenol, spiro[bis(*o*-phenyleneoxyamino)-2-aminophenoxyphosphorane] (III), and iminobis[spiro[bis(*o*-phenyleneoxyamino)-phosphorane]] (II) were monitored during the reaction by thin-layer chromatography, and the products were isolated at the conclusion of the reaction. The following procedure, used for ethyl acetate solvent, is typical.

In ethyl acetate solution, neither II nor III was detected after 4 hr of reaction. After 18 hr, *o*-aminophenol, III, and II were detected by thin-layer chromatography, and the reaction mixture was filtered hot to remove *o*-aminophenol hydrochloride (2.42 g). When the filtrate was cooled, a hygroscopic solid (0.44 g) crystallized out. Removal of solvent from the filtrate at reduced pressure left a semisolid residue. This was extracted with benzene to leave a benzene-insoluble portion which was identified as III (0.29 g) on the basis of infrared,[4] thin-layer chromatography, and mass spectral data. Addition of petroleum ether to the benzene solution precipitated 0.88 g of a mixture of III and II, which could be separated by the technique described previously.

In the fastest reactions (in acetonitrile), after 21 hr of reaction, only a trace of I remained, but at least 1.49 g of III was formed, together with a smaller amount (<0.5 g) of II.

Reactions of Tris(*o*-phenylenedioxy)cyclotriphosphazene (IV) with Mononucleophiles. A suspension of IV (4.60 g, 0.01 mol) in a solution of sodium trifluoroethoxide (0.04 mol) in tetrahydrofuran (100 ml) was stirred at 25°. Solution of IV occurred slowly. After the reaction mixture became homogeneous, the solvent was removed on a rotary evaporator and the residue was washed with water. Hydroxyl, trifluoromethyl, and aromatic groups were identified in the residue by means of infrared spectra. Proton NMR spectra demonstrated the presence of aromatic and methylene hydrogen atoms, and mass spectra indicated the presence of species X, XI, and XII. A red color (λ_{max} 540 mμ) was obtained when the solid was tested with 4-aminoantipyrine, and this was considered evidence for the presence of phenolic hydroxy groups. The solid melted at 120–130° but then resolidified to remelt at 245°, the melting point of IV.

A solution of phenol (1.41 g, 0.015 mol) in xylene (20 ml) was added to a solution of IV (2.3 g, 0.005 mol) in boiling xylene (50 ml). After being heated at reflux for 16 hr, the mixture was cooled and unreacted IV (1.35 g) was removed by filtration. Removal of solvent from the filtrate yielded an oil which, when dissolved in tetrahydrofuran, yielded a small quantity of IV. Removal of the tetrahydrofuran re-formed the oil which, when extracted with *s*-tetrachloroethane, yielded oily crystals. Infrared spectra provided strong evidence for OH, NH, and P=N units.

Solid IV (4.59 g, 0.01 mol) was added to a stirred solution of *n*-propylamine (0.59 g, 0.01 mol) in tetrahydrofuran. Partial solution of IV occurred, and after 4 hr at 25° the unreacted IV (0.77 g) was removed by filtration. Removal of tetrahydrofuran from the filtrate and treatment of the oily residue with benzene yielded crystals of IV. Removal of benzene from the solution yielded a pale yellow oil. Infrared peaks at 3200, 1580, and 1150–1200 cm^{-1} were consistent with a cyclotriphosphazene structure with both phenolic hydroxy groups and alkylamine units. After 24 hr at 25°, the oil crystallized with evolution of *n*-propylamine vapor. The crystals were identified as IV from their infrared spectrum.[3]

A similar result was observed when a suspension of IV (4.59 g, 0.01 mol) in piperidine (0.85 g, 0.01 mol) and tetrahydrofuran (50 ml) was stirred at 25° for 24 hr. In this case, the oily product was dissolved in benzene and deposited crystals of IV from solution during several months.

Reaction of Tris(*o*-phenylenedioxy)cyclotriphosphazene (IV) with Alcohols and Phenols in the Presence of Triethylamine. A solution of phenol (2.82 g, 0.03 mol) and triethylamine (3.0 g, 0.03 mol) in xylene (10 ml) was added to a suspension of IV[3] (2.3 g, 0.005 mol) in xylene (100 ml) and the mixture was heated at reflux for 16 hr. The white solid which crystallized slowly from solution was filtered off and recrystallized from hot dimethylformamide to yield V. The compound was identified by its characteristic infrared spectrum. Similar results were obtained when 4-nitrophenol (4.7 g, 0.034 mol) and triethylamine (3.0 g, 0.03 mol) were allowed to react with IV (2.3 g, 0.005 mol) in boiling xylene (100 ml).

2,2'-Dihydroxybiphenyl (5.5 g, 0.03 mol), triethylamine (3.1 g, 0.03 mol), and IV (2.3 g, 0.005 mol) were allowed to react in boiling tetrahydrofuran (100 ml) for 1.5 hr. Filtration of the hot mixture removed V (0.67 g), and continued heating of the filtrate for 5 hr yielded an additional 0.97 g of V, identified by its infrared spectrum.[3,6] Removal of solvent from the solution yielded a yellow oil which crystallized, especially when treated with ether and benzene, to yield additional V. The total yield of V was 1.93 g (85% yield based on the available phenylenedioxy units). A small amount of oil could not be induced to crystallize. This component contained hydroxyl and aromatic infrared absorptions but gave no evidence of P–N phosphazene absorption.

Compound V was similarly obtained in good yield (1.27 g) when ethanol (1.38 g, 0.03 mol), triethylamine (0.51 g, 0.005 mol), and IV (2.3 g, 0.005 mol) were heated in boiling xylene for 24 hr.

Reaction of Tris(*o*-phenylenedioxy)cyclotriphosphazene (IV) with 2,3-Dihydroxynaphthalene and Triethylamine. A mixture of IV (1.51 g, 0.003 mol), 2,3-dihydroxynaphthalene (1.6 g, 0.01 mol), and triethylamine (2.02 g, 0.02 mol) was allowed to react for 5 min in boiling xylene (100 ml). Ammonia evolution was noticeable during the reaction. Filtration of the hot solution removed a white solid (1.5 g, 67%). An infrared spectrum showed a sharp N–H singlet at 3120 cm^{-1}. A mass spectrum showed a parent ion at *m/e* 509, which corresponded to the molecular weight of XIII, and a base peak at *m/e* 247. Fragments at *m/e* 405, 297, and 101 were also consistent with structure XIII.

Reaction of Iminobis[spiro[bis(*o*-phenyleneoxyamino)phosphorane]] (II) with 2-Amino-4-nitrophenol. 2-Amino-4-nitrophenol (0.77 g, 0.005 mol) was added to a solution of II (0.5 g, 0.001 mol) in xylene (150 ml) and the solution was heated at reflux for 48 hr. The solution was then cooled and filtered. The solvent was evaporated on a rotary evaporator to leave a brown solid, which was washed twice with distilled water and once with hot toluene. The residue was identified as phosphorane VII. The mass spectrum showed a parent ion at *m/e* 398 and a base peak at *m/e* 245. Fragments at *m/e* 290 and 153 were also consistent with structure VII.

Attempted Reaction of Tris(*o*-phenylenedioxy)cyclotriphosphazene (IV) with Catechol or Triethylamine Hydrocbloride. A solution of IV (0.50 g, 0.001 mol) and catechol (0.73 g, 0.0066 mol) in dry xylene (200 ml) was heated at reflux for 48 hr. Some discoloration of the solution occurred, but the starting materials were recovered unchanged. The identity of the recovered IV was confirmed by mass spectrometry. Similarly, a solution of IV (0.50 g, 0.0011 mol) and triethylamine hydrochloride (1.34 g, 0.0099 mol) in xylene (200 ml) was boiled for 48 hr. Compound IV was recovered unchanged.

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Registry No. I, 940-71-6; II, 56403-14-6; III, 21776-56-7; IV, 311-03-5; VII, 56403-15-7; VIII, 3721-13-9; XIII, 56403-81-7; *o*-aminophenol, 95-55-6; sodium trifluoroethoxide, 420-87-1; phenol, 108-95-2; triethylamine, 121-44-8; 4-nitrophenol, 100-02-7; 2,3-dihydroxynaphthalene, 92-44-4; 2-amino-4-nitrophenol, 99-57-0; 2,2'-dihydroxybiphenyl, 1806-29-7; ethanol, 64-17-5; catechol, 120-80-9.

References and Notes

(1) This paper is part XXIV in a series on phosphorus–nitrogen compounds.
(2) Part XXIII: J. L. Schmutz and H. R. Allcock, *Inorg. Chem.*, **14**, 2433 (1975).
(3) H. R. Allcock, *J. Am. Chem. Soc.*, **86**, 2591 (1964).
(4) H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, **91**, 5452 (1969).
(5) H. R. Allcock, "Phosphorus-Nitrogen Compounds", Academic Press, New York, N.Y., 1972, Chapters 6 and 7.
(6) The spiro[phosphate] (i.e., the *hexa*coordinate) structure for V has been deduced by a recent X-ray diffraction study: H. R. Allcock and E. C. Bissell, *J. Am. Chem. Soc.*, **95**, 3154 (1973).
(7) The nitro group is assumed to be attached to the same phenyl ring as the NH_2 group because the mass spectrum of VII showed a strong fragmentation peak at *m/e* 153 which corresponded to a 4-nitro-2-aminooxophenyl fragment.
(8) Smaller amounts of phosphorane III were also detected among the products from this reaction. (The ratio of VII to III in the mass spectrum was ~5:1). This compound may form by prior cleavage of *o*-aminophenol from VII by 4-nitro-2-aminophenol, followed by attack by *o*-aminophenol on VII. Such a process would perhaps be analogous to the formation of V from IV in the presence of alcohols or phenols.

(9) Mass spectra were obtained with the use of an AEI MS 9 spectrometer and infrared spectra were measured on a Perkin-Elmer 621 or Beckman IR5A spectrometer. Thin-layer chromatography was performed on chloroform-impregnated Kieselgel or on Mallinckrodt Chrom AR chromatography sheet with elution by 10% tetrahydrofuran in benzene and detection by ultraviolet light or by development with iodine vapor. Sources and purification methods for chemicals were as described previously.[4]

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Spectra and Structure of Phosphorus–Boron Compounds. XI.[1] Microwave Spectrum, Structure, Dipole Moment, and Barrier to Internal Rotation in Phosphine–Trifluoroborane

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The microwave spectra in the R band of four isotopic symmetric-top species of phosphine–trifluoroborane ($H_3P{\cdot}BF_3$) have been observed. A staggered conformation and r(P–H) = 1.40 Å and ∠HPB = 117° from $H_3P{\cdot}BH_3$ were assumed, and the remaining structural parameters were calculated, by a least-squares fitting of the four observed moments of inertia, to be the following: r(P–B) = 1.921 ± 0.007 Å, r(B–F) = 1.372 ± 0.002 Å, ∠FBP = 106.69 ± 0.38°. The dipole moment was found from Stark splittings to be 3.73 ± 0.30 D in the ground state. The barrier to internal rotation was determined to be 3.39 ± 0.40 kcal/mol by using the relative intensity method. These quantities are compared to corresponding values for related molecules.

Introduction

The addition complexes formed between phosphorus and boron compounds have been investigated for a number of years. The development of a universal theory to explain the bonding in this class of compounds has been hampered by apparent contradictions to classical ideas of bond strengths, bond lengths, and dissociative stabilities. Reliable structures have been determined for a number of molecules from microwave absorption[1,3–6] and vibrational studies have prompted normal-coordinate calculations from which P–B stretching force constants are available.[7–13] Additionally, there are three such studies that deal with phosphine–trihaloboranes.[9,10,13] The calculations incorporate structural parameters[14] and the accuracy of these calculations can depend heavily on the assumed structures that were used. There have been no structures reported for the phosphine–trihaloboranes in the solid or gas phases. It was found that $H_3P{\cdot}BCl_3$ gave no microwave spectrum[13] even though it was reported to be substantially associated in the gas phase with a large dipole moment.[15] Further studies on phosphine–trihaloboranes[9] indicated that $H_3P{\cdot}BF_3$ might be more associated in the gas phase than was $H_3P{\cdot}BCl_3$.

Barriers to internal rotation around P–B bonds have been measured for only a few molecules.[3,5–7,9] In $H_3P{\cdot}BH_3$ and $F_3P{\cdot}BH_3$ the barriers are 2.47[3] and 3.24[5] kcal/mol, respectively. The BH_3 torsional barrier in $CH_3PH_2{\cdot}BH_3$ has been found to be 1.57 kcal/mol.[7] These barriers were calculated from microwave data. From vibrational data in the solid state, barriers were found in $H_3P{\cdot}BBr_3$ (2.96–3.28 kcal/mole[9]) and $B_2Cl_4{\cdot}2PH_3$ (2.92 kcal/mol[16]). A comparison of substituent effects could be made if the barrier in $H_3P{\cdot}BF_3$ were known. These considerations and the possibility of determining the structure of $H_3P{\cdot}BF_3$ have prompted our investigation of the microwave spectra of four isotopic species of this molecule.

Experimental Section

Microwave spectra were recorded in the R band of a Hewlett-Packard Model 8460A MRR spectrometer with a Stark cell modulation frequency of 33.3 kHz. All frequencies were measured with the sample held slightly above Dry Ice temperature (~−70°). To measure the frequencies of very weak lines, time averaging of the spectrum was accomplished with a Varian C-1024 time-averaging computer.

With the exception of those for phosphine, all preparations and purifications were carried out in a standard high-vacuum system employing greaseless stopcocks.[17] Boron trifluoride was obtained commercially (Matheson) and purified by vacuum fractionation until it exhibited a vapor pressure[17] of 301 mm at −112° (CS_2–liquid N_2 slush). Phosphine was prepared under a stream of gaseous nitrogen in a fume hood as described in the literature.[18] Phosphine-d_3 was prepared in a similar manner using D_2O and D_2SO_4. All phosphine species were purified by means of a low-temperature vacuum fractionation column.[19] Purity was monitored by vapor pressure measurements[17] and infrared spectra.[15]

Phosphine–trifluoroborane and phosphine–trifluoroborane-d_3 were prepared[20,21] by condensing equimolar amounts of PH_3 (or PD_3) and BF_3 into an evacuated tube at liquid nitrogen temperatures. The tube was isolated from the vacuum system and allowed to warm slowly to approximately −30°. The tube was then opened to the vacuum system and any unreacted PH_3 or BF_3 was removed under dynamic vacuum at −160° (i-C_5H_{12}–liquid N_2 slush).

Results

The observed transitions for the various isotopic species of the symmetric tops of phosphine–trifluoroborane are listed in Table I. These were assigned by comparing their spacings to those predicted from an initial structure. The spectra were fitted to the equation

$$\nu_{J,J+1} = 2B_0(J+1) - 4D_J(J+1)^3$$

Individual values for B_0 and D_J are also listed in Table I. No contribution from a D_{JK} term could be resolved. The only observed vibrational satellite was assigned to the torsional mode. A partial structure was obtained from the rotational constants listed in Table I. The structure of the phosphine end of the molecule was assumed and constrained in all structural calculations. The three remaining structural parameters, for the assumed staggered conformation, were obtained by an iterative least-squares fitting to the four observed moments of inertia. The program allows one to choose weighting factors for the input moments. The structural parameters in Table II correspond to weighting factors of 1.0 for $H_3P{\cdot}^{11}BF_3$ and 0.5 for the other three species. This was