40, 112597-98-5; 41, 112597-99-6; 42, 112598-00-2; 43, 112598-01-3; 44, 112598-02-4; 45, 112598-03-5; 46, 112598-04-6; 47, 112598-05-7; 48, 112598-06-8; 49, 112598-07-9; 50, 112598-08-0; 51, 112598-09-1; 52, 98901-76-9; 53, 112598-10-4; 54, 112598-11-5; 55, 98901-74-7; 56, 112598-12-6; 57, 112598-13-7; 58, 112598-14-8; 59, 98901-75-8; 60, 112598-15-9; 61, 112598-16-0; 62, 112598-17-1; (4-hydroxyphenoxy)acetaldehyde diethyl acetal, 14353-62-9; hydroquinone, 123-31-9; (4-bromophenoxy)acetaldehyde diethyl acetal, 112598-18-2; 4-bromophenol, 106-41-2; bromoacetaldehyde diethyl acetal, 2032-35-1; (4-phenoxyphenoxy)acetaldehyde diethyl acetal, 53593-05-8; (4-benzylphenoxy)acetaldehyde diethyl acetal, 98901-73-6; 3-chloropropionaldehyde diethyl acetal, 35573-93-4.

Supplementary Material Available: Table of analytical data for ω-(4-phenoxyphenoxy)- and ω-(4-benzylphenoxy)alkanaldoxime *O*-ethers (2 pages). Ordering information is given on any current masthead page.

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Synthesis of Phenoxyaminocyclotriphosphazatrienes

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The following phosphazene compounds were synthesized for study as urease inhibitors: 2-phenoxy-2,4,4,6,6-pentaaminocyclotriphosphazatriene (**1**), *cis*-2,4-diphenoxy-2,4,6,6-tetraaminocyclotriphosphazatriene (**2**), *trans*-2,4-diphenoxy-2,4,6,6-tetraaminocyclotriphosphazatriene (**3**), *cis,trans*-2,4,6-triphenoxy-2,4,6-triaminocyclotriphosphazatriene (**4**), *cis,cis*-2,4,6-triphenoxy-2,4,6-triaminocyclotriphosphazatriene (**5**). These compounds were characterized by elemental analysis, high-performance liquid chromatography, infrared absorption spectroscopy, and nuclear magnetic resonance spectroscopy.

The enzymatic hydrolysis of urea fertilizer in the soil leads to the loss of nitrogen via ammonia volatilization; losses of up to 50% of the applied nitrogen occur in flooded soil systems such as paddy rice (Vlek and Craswell, 1981). One approach to reducing ammonia losses is the use of fertilizers that contain compounds that inhibit soil urease activity and retard urea hydrolysis. Phenoxyaminocyclotriphosphazatrienes are presently being investigated as soil urease inhibitors.

In the last three decades, significant progress has been made in several phases of phosphazene chemistry. Specifically, much research work has been focused on the chemical reactions of hexachlorocyclotriphosphazatriene ($N_3P_3Cl_6$), spectroscopic studies, molecular structure, bonding in the cyclophosphazenes, and the development of cyclic oligomers and open-chain polyphosphazenes. Several reviews have been written on phosphazene chemistry: Allcock (1972), Keat and Shaw (1973), Shaw (1975), Krishnamurthy et al. (1978), Shaw (1978).

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The six-membered ring system has been studied more intensively than any other phosphazene. X-ray crystallographic analyses of $N_3P_3F_6$ (Dougill, 1963) and $N_3P_3Cl_6$ (Wilson and Carroll, 1960) show that the rings are planar; the geometry of the cyclophosphazene ring is determind by the number, type, and arrangement of substituents (Mani et al., 1965, 1966; Shaw, 1975, 1978).

Many organophosphazenes have been synthesized by nucleophilic substitutions of hexachlorocyclotriphosphazatriene (Allcock et al., 1966; Allcock and Kugel, 1965; Allcock and Smeltz, 1976; Dell et al., 1966; Fitzsimmons and Shaw, 1964; Ford et al., 1966; Shaw, 1967). In the synthesis of phenoxy- and (*p*-bromophenoxy)-chlorocyclotriphosphazatrienes, the degrees of replacement of chlorine atoms have been determined and show that the replacement pattern is nongeminal; thus, both cis and trans isomers are formed (Dell et al., 1965, 1966).

In this paper we describe the syntheses of the following compounds: 2-phenoxy-2,4,4,6,6-pentaaminocyclotriphosphazatriene (**1**), *cis*-2,4-diphenoxy-2,4,6,6-tetraaminocyclotriphosphazatriene (**2**), *trans*-2,4-diphenoxy-2,4,6,6-tetraaminocyclotriphosphazatriene (**3**), *cis,trans*-2,4,6-triphenoxy-2,4,6-triaminocyclotriphosphazatriene (**4**), *cis,cis*-2,4,6-triphenoxy-2,4,6-triaminocyclotriphosphazatriene (**5**).

The modification of a synthetic route employed in the synthesis of triphenoxytriaminocyclotriphosphazatrienes was used in this work; the aminolysis reaction was performed in a Parr pressure reaction apparatus with use of

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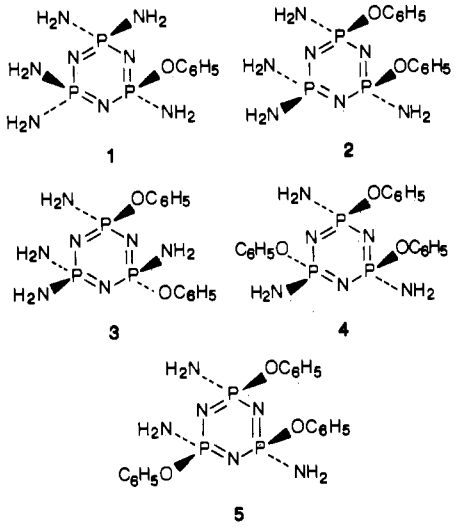


anhydrous ammonia rather than in inert solvents at atmospheric pressure. The yields of purified products obtained in the present work were 100% higher than those reported earlier (Albright and Wilson, 1963; McBee et al., 1966).

EXPERIMENTAL SECTION

Apparatus. The aminolysis of the phenoxychlorocyclotriphosphazatrienes was performed in a 300-mL, type 316 stainless steel, Parr pressure reaction apparatus (No. 4561) equipped with an internal mechanical stirrer driven at a 600-rpm stirring speed.

Reagents. Sodium metal (Fisher Scientific Co., certified ACS grade), hexachlorocyclotriphosphazatriene (Aldrich Chemical Co., 99%), petroleum ether (J. T. Baker Chemical Co., 30–75 °C), phenol (Aldrich, ACS reagent, 99+%), and anhydrous ammonia (Matheson, 99.99%) were used as received. Tetrahydrofuran (Fisher, high-performance liquid chromatography (HPLC) grade, 99.9%) was dried with Dri-Na (J. T. Baker, 10% sodium and 90% lead as alloy).

2-Phenoxy-2,4,4,6,6-pentachlorocyclotriphosphazatriene (**6**), *cis*- and *trans*-2,4-diphenoxy-2,4,6,6-tetrachlorocyclotriphosphazatriene (**7**, **8**), and *cis,cis*- and *cis,trans*-2,4,6-triphenoxy-2,4,6-trichlorocyclotriphosphazatriene (**9**, **10**) were prepared by reacting hexachlorocyclotriphosphazatriene with sodium phenoxide according to the method of Dell, Fitzsimmons, and Shaw (1965). The yields were 65%, 78%, and 88%, respectively. The elemental analysis data are listed in Table I.

Procedures. Elemental analysis (Table I), infrared (IR) absorption spectra (Table II), nuclear magnetic resonance (NMR) spectra (Table III), and HPLC (Table IV) were used to determine the purity and/or the probable chemical structures of the starting materials and the phenoxyaminocyclotriphosphazatrienes. The elemental analyses were performed by Galbraith Laboratories, Inc., P.O. Box 4187, Knoxville, TN 37921. The analytical HPLC equipment used was a Perkin-Elmer Series 2-LC, a Perkin-Elmer LC-55 UV spectrophotometer (set at 200 nm), a Waters Associates RCM-100 radial compression module, and a Waters Associates Resolve 8CN10 Radial-Pak cartridge. The mobile phase was 50% methanol/water containing Waters Associates D-4 mobile phase modifier adjusted to pH 3, and the flow rate was 2 mL/min. The methanol used in chromatography was HPLC grade; the solvents were filtered (0.2 μm) before use. IR spectra of the phenoxyaminocyclotriphosphazatrienes were obtained in the 4000–200-cm^{-1} range as KBr disks on a Perkin-Elmer Model 283 IR spectrometer. NMR spectra were obtained with a JEOL FX-90 QII multinuclear magnetic resonance spectrometer. ^1H NMR spectra were obtained on a wide-band (10-mm) probe at 89.55 MHz using a 16K data table, 1501-Hz frequency width, and 8 scans at a pulse width of 9 μs and a pulse delay of 2.5 s. ^{31}P NMR spectra were recorded with a wide-band (10-mm) probe at 36.23 MHz and an 8K data table, 1501-Hz frequency width, and 200–300 scans at a pulse width of 9.5 μs and a pulse delay of 2.5 s. ^1H decoupling was performed only during the acquisition with a wide-band decoupler. Tetramethylsilane (TMS) was used as an internal reference for the ^1H spectra; dilute H_3PO_4 was used as an external reference for the ^{31}P spectra. The ^1H and ^{31}P NMR spectra of the phenoxyaminocyclotriphosphazatrienes were recorded in DMSO-d_6.

2-Phenoxy-2,4,4,6,6-pentaaminocyclotriphosphazatriene (1). The aminolysis of 2-phenoxy-2,4,4,6,6-pentachlorocyclotriphosphazatriene (40.0 g, 0.099 mol) was performed in a Parr bomb. The phosphazene compound was placed in the bomb, the bomb head was secured in place, and the bomb was purged with dry nitrogen. Anhydrous liquid ammonia (150 g) was condensed in the bomb by connecting it to a cylinder of anhydrous ammonia and placing it in a Dewar flask of liquid nitrogen. The contents of the bomb were stirred for 24 h at room temperature. The excess NH_3 was vented, and the crude product, a white solid, was removed from the bomb. The yield of crude product was 56 g (98.4%). The reaction products were separated by reacting NH_4Cl with diethylamine in dry chloroform to form ammonia and diethylammonium chloride according to the method of Sowerby and Audrieth (1961).

The yield of purified product, a white solid, was 26.2 g (97.9%). The product, analyzed by HPLC (Table IV), was 92% compound 1. The product (15 g) was recrystallized from anhydrous reagent alcohol (90% ethanol, 5% methanol, 5% 2-propanol; 5 L). The yield was 13.3 g of chromatographically pure compound 1. The elemental analysis, IR, NMR, and HPLC data are shown in Tables I–IV, respectively.

2,4-Diphenoxy-2,4,6,6-tetraaminocyclotriphosphazatrienes 2 and 3. The 2,4-diphenoxy-2,4,6,6-tetrachlorocyclotriphosphazatriene (40.0 g, 0.086 mol; mixture of cis and trans isomers) was reacted with anhydrous liquid ammonia (150 g) by the procedure described for compound 1. The yield of crude product was 51.7 g (99.9%). The NH_4Cl was removed with diethylamine (Sowerby and Audrieth, 1961) to yield 31.6 g (95.1%) of a white solid. The diethylamine-treated product was analyzed by HPLC (Table IV) as described above. Two peaks were present in the chromatogram; the retention times were 4.55 and 3.77 min for compounds **2** and **3**, respectively. The chromatographically pure compound **2** (17.5 g) was separated by filtration after recrystallization of the mixture of compounds **2** and **3** (30 g) from anhydrous reagent alcohol (7 L). The chromatographically pure compound **3** (1.37 g) was isolated from the filtrate after partial evaporation of the solvent under vacuum and several recrystallizations from anhydrous reagent alcohol. The elemental analysis, IR, NMR, and HPLC data are listed in Tables I–IV, respectively.

2,4,6-Triphenoxy-2,4,6-triaminocyclotriphosphazatrienes 4 and 5. The aminolysis of 2,4,6-triphenoxy-2,4,6-trichlorocyclotriphosphazatriene (40.0 g, 0.077 mol; mixture of cis,cis and cis,trans isomers) with anhydrous liquid ammonia (150 g) was conducted by the method described above. The yield of crude product was 46.6 g (97.2%). The crude product was refluxed with diethylamine (Sowerby and Audrieth, 1961) to yield 30.2 g

Table I. Elemental Analyses of Cyclotriphosphazatrienes

compound	analysis, % C	H	N	P	Cl
$N_3P_3(NH_2)_5(OC_6H_5)$ (1)					
calcd	23.38	4.92	36.36	30.15	0
found	23.27	4.93	36.08	29.98	0.12
cis-$N_3P_3(NH_2)_4(OC_6H_5)_2$ (2)					
calcd	37.41	4.72	25.45	24.11	0
found	37.14	4.66	25.59	24.19	0.095
trans-$N_3P_3(NH_2)_4(OC_6H_5)_2$ (3)					
calcd	37.41	4.72	25.45	24.11	0
found	37.33	4.73	25.40	23.90	0.13
cis,trans-$N_3P_3(NH_2)_3(OC_6H_5)_3$ (4)					
calcd	46.76	4.59	18.18	20.09	0
found	46.64	4.58	18.06	20.91	0.091
cis,cis-$N_3P_3(NH_2)_3(OC_6H_5)_3$ (5)					
calcd	46.76	4.59	18.18	20.09	0
found	46.54	4.61	18.38	19.88	0.13
$N_3P_3Cl_5(OC_6H_5)$ (6)					
calcd	17.78	1.25	10.37	22.92	43.73
found	18.02	1.20	10.33	22.62	43.87
$N_3P_3Cl_4(OC_6H_5)_2$ (7/8)[a]					
calcd	31.13	2.18	9.08	20.07	30.63
found	31.69	2.35	9.02	19.99	30.68
$N_3P_3Cl_3(OC_6H_5)_3$ (9/10)[b]					
calcd	41.52	2.91	8.07	17.85	20.43
found	41.76	2.93	8.15	18.05	20.60

[a] Mixture of cis and trans isomers. [b] Mixture of cis,cis and cis,trans isomers.

Table II. Infrared Absorption Spectra (4000–200 cm^{-1}) of Phenoxy-Substituted Cyclotriphosphazatrienes[a]

$N_3P_3(NH_2)_5(OC_6H_5)$ (1)	assignment
3280 s	ν(N—H), str
3070 w	ν(C—H), aromatic str
1595 m, 1495 s	ν(C=C), aromatic str
1555 m	σ(N—H), scissoring deformn
1222 s	ν(P—O—C), str
1170 s	ν(P=N), str in plane

cis-$N_3P_3(NH_2)_4(OC_6H_5)_2$ (2)	*trans*-$N_3P_3(NH_2)_4(OC_6H_5)_2$ (3)	
3210 s	3210 s	ν(N—H), str
3070 w	3070 w	ν(C—H), aromatic str
1595 m, 1495 s	1595 m, 1492 s	ν(C=C), aromatic str
1558 m	1557 m	σ(N—H), scissoring deformn
1220 s	1230 s	ν(P—O—C), str
1175 s	1180 s	ν(P=N), str in plane

cis,trans-$N_3P_3(NH_2)_3(OC_6H_5)_3$ (4)	*cis,cis*-$N_3P_3(NH_2)_3(OC_6H_5)_3$ (5)	
3215 m	3290 m	ν(N—H), str
3070 w	3070 w	ν(C—H), aromatic str
1597 m, 1493 s	1600 m, 1493 s	ν(C=C), aromatic str
1560 m	1550 m	σ(N—H), scissoring deformn
1235 s	1220 s	ν(P—O—C), str
1175 s	1180 s	ν(P=N), str in plane

[a] Abbreviations: s = strong, m = medium, w = weak.

(84.9%) of purified product.

The purified product, a white solid, was analyzed by HPLC (Table IV). Only two peaks were evident in the chromatogram; the retention times for compounds 4 and 5 were 6.08 and 8.32 min, respectively. Compounds 4 and 5 were separated from the mixture of these compounds by the method used to separate compounds 2 and 3. The mixture (12 g) was recrystallized from reagent alcohol (1.2 L) to yield 6.6 g of chromatographically pure compound 4 and 1.3 g of chromatographically pure compound 5. The elemental analysis, IR, NMR, and HPLC data for compounds 4 and 5 are listed in Tables I–IV, respectively.

RESULTS AND DISCUSSION

IR Spectra of Phenoxyaminocyclotriphosphazatrienes. The IR absorption spectra (Table II) of the phenoxyaminocyclotriphosphazatrienes exhibited absorption frequencies very similar to those of 2,2,4,4,6,6-hexaaminocyclotriphosphazatriene (Sowerby and Audrieth, 1961) plus the characteristic phenoxy bands. The absorption values of the amino group frequencies decreased, and the phenoxy group frequencies increased with an increase in the degree of phenoxy substitution.

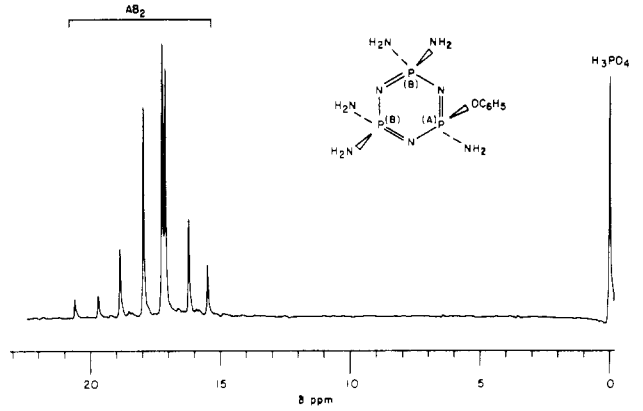


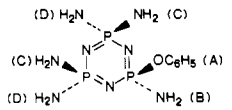
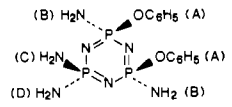
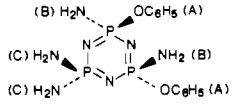
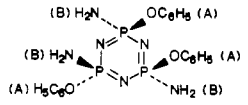
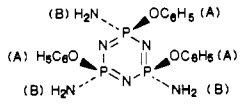
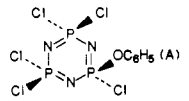
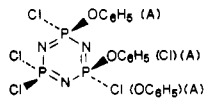
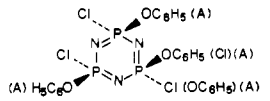
Figure 1. ^{31}P NMR spectrum of 2-phenoxy-2,4,4,6,6-pentaaminocyclotriphosphazatriene showing typical AB_2 splitting pattern.

^{31}P NMR Spectra of 2-Phenoxy-2,4,4,6,6-pentaaminocyclotriphosphazatriene. Figure 1 shows the ^{31}P NMR spectrum of 2-phenoxy-2,4,4,6,6-pentaaminocyclotriphosphazatriene (1). It is apparent that compound 1 exhibits a non-first-order splitting pattern. This type of splitting pattern is commonly found in proton (^1H) NMR spectra but is rare among phosphorus compounds. Non-first-order splitting patterns generally occur when the value of the coupling constant, J, approaches the difference in chemical shift of the coupled nuclei. Only one example in the recent literature makes reference to an A_2B non-first-order spectrum, and it also is in an alkoxyamidocyclotriphosphazatriene system (Fincham et al., 1985).

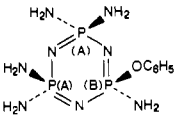
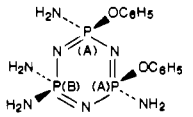
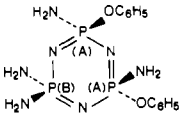
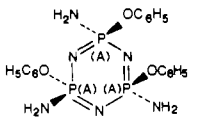
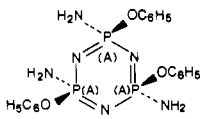
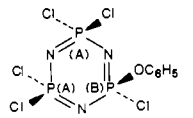
The same basic assumptions hold for AB_2 (or A_2B) spectral analysis of ^{31}P NMR spectra as for ^1H NMR spectra (Emsley et al., 1965). The ^{31}P NMR spectrum of

Table III. NMR Spectral Data

^{1}H NMR Data of Phenoxy-Substituted Cyclotriphosphazatrienes

compound	structure	stereochem	proton	ppm	area	peak shape	solvent
1			B	3.79	2	br s	99.96% DMSO-d_6 + TMS
			C	3.18	4	br s	
			D	2.87	4	br s	
			A	7.22	5	m with dominant s	
2			B	3.98	4	br s	99.96% DMSO-d_6 + TMS
			C	3.32	2	br s	
			D	2.77	2	br s	
		cis	A	7.12	10	m with 2 dominant s	
3			B	3.90	4	br s	99.96% DMSO-d_6 + TMS
			C	2.96	4	br s	
		trans	A	7.23	10	m with 1 dominant s	
4			B	4.10	6	br s	99.96% DMSO-d_6 + TMS
			A	7.25		m with 3 dominant s	
			A	7.16	15		
		cis,trans	A	7.13			
5			B	4.24	6	br s	99.96% DMSO-d_6 + TMS
			A	7.17		m with 2 dominant s, 1 minor s	
			A	7.107	15		
		cis,cis	A	7.06			
6			A	7.35		m	$CDCl_3$ + TMS
7, 8[a]			A	7.29	3	br peak, 2 s	$CDCl_3$ + TMS
			A	7.22	2		
9, 10[b]			A	7.32	2	overlapping peaks, 3 major s	$CDCl_3$ + TMS
			A	7.27	3		
			A	7.25	1		

^{31}P NMR Spectral Data of Phenoxy-Substituted Cyclotriphosphazatrienes

compound	structure	stereochem	peak	ppm	coupling const, Hz	solvent
1			A	18.85	$J_{A,B}$ = 36.66	99.96% DMSO-d_6
			B	16.73		
2		cis	A	18.05	$J_{A,B}$ = 32.2	99.96% DMSO-d_6
			B	16.4		
3		trans	A	18.15	$J_{A,B}$ = 32.6	99.96% DMSO-d_6
			B	16.46		
4		cis,trans	A	17.508		99.96% DMSO-d_6
5		cis,cis	A	17.508		99.96% DMSO-d_6
6			A	21.78	$J_{A,B}$ = 64.8	$CDCl_3$
			B	13.0		

[a] Mixture of cis and trans isomers. [b] Mixture of cis,cis and cis,trans isomers.

Table IV. HPLC Analyses of Phenoxyaminocyclotriphosphazatrienes

compound	ret time, min	compn, %	cis/trans
$N_3P_3(NH_2)_5(OC_6H_5)$ (1)	2.55	92	
cis-$N_3P_3(NH_2)_4(OC_6H_5)_2$ (2)[a]	4.55	72.2	2.6
trans-$N_3P_3(NH_2)_4(OC_6H_5)_2$ (3)[a]	3.77	27.8	
cis,trans-$N_3P_3(NH_2)_3(OC_6H_5)_3$ (4)[b]	6.08	64.4	0.55
cis,cis-$N_3P_3(NH_2)_3(OC_6H_5)_3$ (5)[b]	8.32	35.6	

[a] Mixture of cis and trans isomers. [b] Mixture of cis,cis and cis,trans isomers.

compound 1 closely resembles the ^1H AB_2 non-first-order spin systems where the ratio of the coupling constant to the product of the nuclear precision frequency and the difference of the chemical shifts of the A and B phosphorus nuclei $[J/\upsilon_0(\delta_A - \delta_B)]$ is about 0.5.

Several theoretical principles (Paudler, 1971) hold for this type of spin system involving three nuclei:

1. From the equations for the transition energies and relative intensities for the AB_2 system, band 3 (for $\delta_A > \delta_B$) gives the true chemical shift of the A nucleus.
2. The true chemical shift of the B nucleus is given by the mean position of bands 5 and 7 (again for $\delta_A > \delta_B$).
3. It is possible to determine which of the nuclei in the AB_2 system is the more shielded, but the sign of the coupling constant cannot be determined.
4. For well-resolved spectra, the value of J can be calculated by summing eq 1 and 2 and solving iteratively for J, where δ_3 = position of peak 3 in MHz, δ_5 = position of peak 5 in MHz, δ_7 = position of peak 7 in MHz, δ_A = chemical shift of the A nucleus in MHz, δ_B = chemical shift of the B nucleus in MHz, and $\upsilon_0 = \gamma H_0/2\pi = 36.272\,772\,3$ MHz.

$$\delta_3 - \delta_5 = \upsilon_0(\delta_B - \delta_A) - \tfrac{1}{2}\{\upsilon_0(\delta_B - \delta_A)^2 + [\upsilon_0(\delta_B - \delta_A)J] + \tfrac{9}{4}J^2\}^{1/2} + \tfrac{1}{2}\{\upsilon_0(\delta_B - \delta_A)^2 - [\upsilon_0(\delta_B - \delta_A)J] + \tfrac{9}{4}J^2\}^{1/2} \quad (1)$$

$$\delta_3 - \delta_7 = \upsilon_0(\delta_B - \delta_A) + \tfrac{1}{2}\{\upsilon_0(\delta_B - \delta_A)^2 + [\upsilon_0(\delta_B - \delta_A)J] + \tfrac{9}{4}J^2\}^{1/2} - \tfrac{1}{2}\{\upsilon_0(\delta_B - \delta_A)^2 - [\upsilon_0(\delta_B - \delta_A)J] + \tfrac{9}{4}J^2\}^{1/2} \quad (2)$$

Table V gives the peak positions and relative intensities for the ^{31}P NMR spectrum of compound 1. From the above set of equations and assumptions, the chemical shift of the A nucleus ($PNH_2OC_6H_5$) is 18.85 ppm; the chemical shift of the B nuclei [$P(NH_2)_2$] is 16.73 ppm; the coupling constant, $J_{A,B}$, is 36.6 Hz (Table III).

Conformational Analysis of Substituted Cyclotriphosphazatrienes by ^{31}P and ^1H NMR Spectroscopy. The synthetic approach used to prepare the diphenoxy- (eq 3) and triphenoxytriaminocyclotriphosphazatrienes (eq 4) produces a mixture of products with two major components in each case. In the past, this synthetic route generally has resulted in nongeminal substitution of the cyclotriphosphazatriene ring system. It was found that these components could be separated by HPLC and recrystallization techniques.

$$N_3P_3Cl_6 + 2NaOC_6H_5 \rightarrow [N_3P_3Cl_4(OC_6H_5)_2] \xrightarrow{NH_3} \underset{\text{mixture}}{[N_3P_3(NH_2)_4(OC_6H_5)_2] + [N_3P_3(NH_2)_4(OC_6H_5)_2]} \quad (3)$$
$$\text{70\% isomer I} \qquad \text{30\% isomer II}$$

$$N_3P_3Cl_6 + 3NaOC_6H_5 \rightarrow [N_3P_3Cl_3(OC_6H_5)_3] \xrightarrow{NH_3} \underset{\text{mixture}}{[N_3P_3(NH_2)_3(OC_6H_5)_3] + [N_3P_3(NH_2)_3(OC_6H_5)_3]} \quad (4)$$
$$\text{60\% isomer I} \qquad \text{40\% isomer II}$$

Table V. ^{31}P NMR Spectral Peak Positions and Relative Intensities for 2-Phenoxy-2,4,4,6,6-pentaaminocyclotriphosphazatriene[a]

peak no.	peak position, Hz	peak position, ppm	rel intensity, % init	rel intensity, % calcd[b]
1	747.2	20.599	612	0.326 748
2	714.58	19.7	702	0.374 799
3	683.8	18.852	1873	1
4	651.19	17.952	5300	2.829 684
5	625.17	17.235	6834	3.648 691
6	621.14	17.124	6066	3.238 654
7	588.52	16.225	2540	1.356 113
8	562.14	15.497	1383	0.738 387

[a] Spectra recorded as 50 mg/2-mL samples in 99.96% DMSO-d_6 at 25 °C and 36.23 MHz using the following parameters: 8K data points, 9.5-μs pulse width, 2.5-s pulse delay, 2500-Hz frequency width, and ^1H decoupling only during the acquisition phase. External H_3PO_4 was used as the reference. [b] Calculated intensities are based on theoretical assignment of the third A peak being equal to unity.

The reaction of the hexachloride, $N_3P_3Cl_6$, with primary and secondary amines has produced the largest class of cyclotriphosphazatriene derivatives (Allcock, 1972; Keat and Shaw, 1973). Replacement of the chlorine atoms by amino groups has demonstrated that most amines exhibit a characteristic reaction pattern, i.e., geminal or nongeminal (Shaw, 1976). Although the reactions produce both geminal and nongeminal products, usually one species is the major product. In reactions of primary amines with $N_3P_3Cl_6$, when the affinity between the phosphorus compound and the amine is high, the product is nongeminal; if the affinity if low, geminal products are obtained. In reactions of secondary amines with $N_3P_3Cl_6$, the products are predominantly nongeminal; the ratio of cis and trans nongeminal isomers also varies (Shaw, 1980). In the case of ammonia, the monoamino pentachloride, $N_3P_3Cl_5NH_2$, has only been synthesized by deammonolysis of the bis compound, $N_3P_3Cl_4(NH_2)_2$, which demonstrates a geminal pattern. Less information is available about the reactions of $N_3P_3Cl_6$ with ammonia, partially because of experimental problems (DeFicquelmont, 1939; Feistel and Moeller, 1967; Lehr, 1967; Shaw, 1976).

The ^{31}P NMR data of both isomers of the diphenoxycyclotriphosphazatriene are shown in Table III. Again, we see a similar type of non-first-order spin system, but now there are two of the more deshielded nuclei, giving A_2B-type spectra. As with compound 1, analysis of the peak positions and relative intensities gives the chemical shifts of both the A and B nuclei and the corresponding coupling constants (Table III). Although it is obvious from these data that both isomers are ring-type compounds, it is not possible to determine whether the conformation is either a cis or trans isomer on the basis of its ^{31}P NMR spectrum.

The ^1H NMR spectra of both isomers obtained in the synthesis of the diphenoxytetraaminocyclotriphosphazatrienes are shown in Figure 2, and the peak positions and relative intensities are given in Table III. From the data in Table III, the conformation of both isomers can be easily assigned. The predominant isomer formed in the synthesis is *cis*-2,4-diphenoxy-2,4,6,6-tetraaminocyclotriphosphazatriene (2), and the minor isomer is *trans*-2,4-diphenoxy-2,4,6,6-tetraaminocyclotriphosphazatriene (3).

This isomer ratio is not what one would have expected, given the bulkiness of the phenoxy ring and the apparent steric hindrance to cis substitution. However, if a model of this ring system is examined (Figure 3), it can be seen that the two cis phenoxy rings can exist in a conformation allowing the π clouds of both rings to interact and mix.

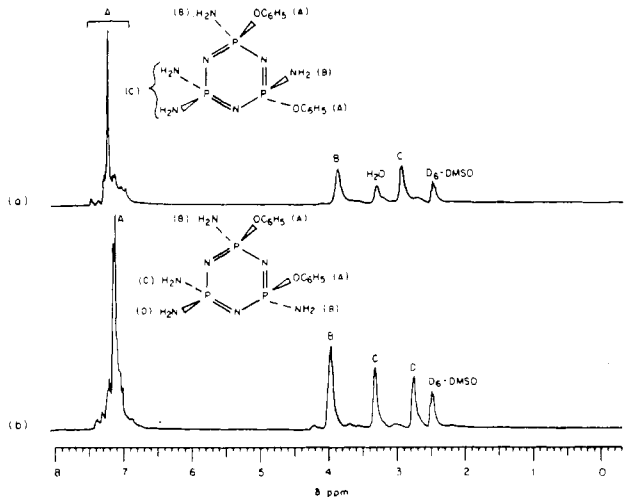


Figure 2. ^1H NMR spectra of (a) *trans*-2,4-diphenoxy-2,4,6,6-tetraaminocyclotriphosphazatriene and (b) *cis*-2,4-diphenoxy-2,4,6,6-tetraaminocyclotriphosphazatriene.

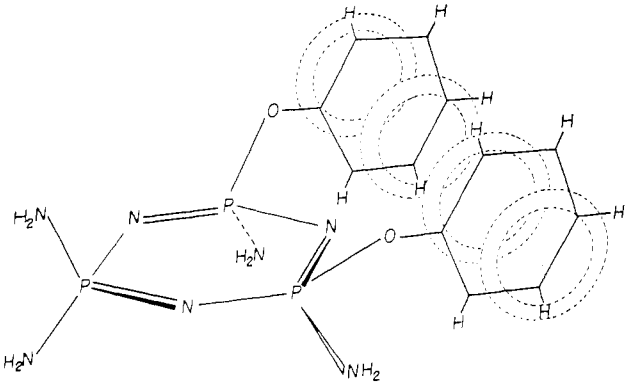


Figure 3. Perspective drawing of interaction of phenyl ring π clouds in *cis*-2,4-diphenoxy-2,4,6,6-tetraaminocyclotriphosphazatriene.

This interaction also is evidenced by the upfield shift of the phenyl protons on going from the trans isomer to the cis isomer.

A similar situation exists in the case of the triphenoxytriaminocyclotriphosphazatrienes. Again, two major isomers are formed during the synthesis. The ^{31}P NMR data of both isomers (Table III) exhibit only a singlet, as is expected for nongeminally substituted isomers. The ^1H NMR spectra of both isomers (Figure 4) are difficult to assign because the amide hydrogens provide only one peak, again supporting a nongeminally substituted isomer.

However, careful examination of the ^1H spectra of compounds **2** and **3** (Figure 2) provides a powerful clue to the assignment of the conformation of the trisubstituted isomers. Note that in the spectra of compound **2** a strong peak split into a partial doublet is seen, whereas in compound **3** this strong singlet is not split and is further deshielded. The predominant isomer obtained from the synthesis of the trisubstituted products exhibits both of these features, while the minor component exhibits one major and two minor singlets in this region. On the basis of these similarities, the major isomer has been assigned the cis,trans conformation and the minor isomer has been assigned the cis,cis conformation.

Samples of the phenoxy-substituted chlorocyclotriphosphazatrienes also were examined. Except for the 2-phenoxy-2,4,4,6,6-pentachlorocyclotriphosphazatriene, these materials consisted of mixtures that could not adequately be resolved. Preliminary examination of the ^{31}P NMR spectra of these compounds indicates that they also

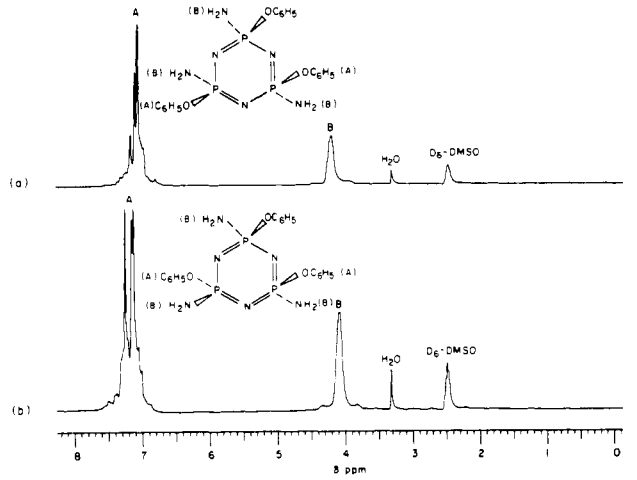


Figure 4. ^1H NMR spectra of (a) *cis,cis*-2,4,6-triphenoxy-2,4,6-triaminocyclotriphosphazatriene and (b) *cis,trans*-2,4,6-triphenoxy-2,4,6-triaminocyclotriphosphazatriene.

exhibit non-first-order spin systems.

Recent studies of the cyclophosphazene compounds described in this paper have shown that they inhibit the enzymatic hydrolysis of urea in unsaturated soil systems. These compounds were evaluated by soil incubation experiments (laboratory) in well-mixed systems for a period of 35 days or more for their performance as sustained-action soil urease inhibitors, and the results are reported by Savant et al. (1988).

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Evaluation of Phenoxyaminocyclotriphosphazatrienes as Sustained-Action Soil Urease Inhibitors

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Laboratory incubation experiments were conducted over a period of 36 days to evaluate soil urease inhibition with time at 30 °C by the phenoxy derivatives of the phosphazene compound 2,2,4,4,6,6-hexaaminocyclotriphosphazatriene. The derivatives were (1) 2-phenoxy-2,4,4,6,6-pentaaminocyclotriphosphazatriene, (2) 2,4-diphenoxy-2,4,6,6-tetraaminocyclotriphosphazatriene, and (3) 2,4,6-triphenoxy-2,4,6-triaminocyclotriphosphazatriene. After the first 16-h incubation (immediate inhibition), the monophenoxyphosphazene exhibited a 95% inhibition, whereas the triphenoxyphosphazene only inhibited 22%; the compound phenyl phosphorodiamidate, by comparison, inhibited 100%. The immediate inhibition by the phosphazene compounds decreased with an increase in the number of phenoxy substitutions. The sustained inhibition (more than 4 days), which ranged from 40% to 95%, tended to increase with an increase in the number of phenoxy substitutions but tended to decrease with an increase in incubation temperatures from 20 to 40 °C.

Ammonia volatilization losses from broadcast urea on unsaturated soils can be serious (Terman, 1979) and can result in significantly decreased nitrogen use efficiency. One approach to increasing N use efficiency is to use urea amended with a chemical compound to retard its rapid hydrolysis (Sahrawat, 1980; Mulvaney and Bremner, 1981; Hauck, 1984). This approach has received much attention in the last 10–12 years, and several organic, inorganic, synthetic, and natural chemical compounds have been tested (Sahrawat, 1980; Mulvaney and Bremner, 1981; Liao and Raines, 1982; Martens and Bremner, 1984; Bremner and Chai, 1986). Of the compounds tested, phenyl phosphorodiamidate (PPDA) (Held et al., 1976; Martens and Bremner, 1984) and *N*-(*n*-butyl)thiophosphoric triamide (Bremner and Chai, 1986) have been reported to exhibit high soil urease inhibition.

In an attempt to identify effective sustained-action urease inhibitors, Peters et al. (1988) recently synthesized and characterized three phosphazene compounds: (1) 2-phenoxy-2,4,4,6,6-pentaaminocyclotriphosphazatriene (2) 2,4-diphenoxy-2,4,6,6-tetraaminocyclotriphosphazatriene, and (3) 2,4,6-triphenoxy-2,4,6-triaminocyclotriphosphazatriene.

These compounds were in fact developed essentially for retarding hydrolysis of broadcast urea in floodwater and at the floodwater–soil interface of submerged rice soils. We therefore first conducted preliminary investigations on soil urease inhibition properties of these compounds using a Crowley soil incubated under unsaturated conditions. In this paper, we reported these preliminary data on the temporal changes in soil urease inhibition by three phosphazene compounds. In separate studies conducted using several different submerged soils incubated in the greenhouse (without rice plants), we have also studied the inhibitory effects of these compounds on urea hydrolysis in floodwater and at the floodwater–soil interface, and the relevant data will be reported elsewhere.

MATERIALS

The three phosphazene compounds synthesized and characterized by Peters et al. (1988) were used (Table I). For comparison purposes, phenyl phosphorodiamidate supplied by ICN Pharmaceuticals (Plainview, NY) and recrystallized twice from ethanol; 2,2,4,4,6,6-hexaaminocyclotriphosphazatriene, prepared according to the procedure described by Sowerby and Audrieth (1961); and phosphoryl triamide prepared according to the procedure described by Klement and Nielsen (1960) were also included in this study (Table I).

An air-dried surface soil sample (0–15 cm, <2 mm) of Crowley silt loam (Typic Albaqualf, fine montmorillonitic, thermic) was used: pH (H_2O), 6.3; organic matter, 1.7%; cation-exchange capacity (CEC), 16.2 mequiv/100 g; urease activity, ≅18 μg of urea hydrolyzed/g per h (near field capacity and at 30 °C).

EXPERIMENTAL PROCEDURE

In order to study the temporal changes in soil urease inhibition by a chemical compound or a mixture of compounds in a well-mixed soil system, the following procedure

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