

CONTRIBUTION FROM THE CHEMICAL DEPARTMENT,  
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## Phosponitrilic Compounds. V.<sup>1</sup> Cyclized Products from the Reactions of Hexachlorocyclotriphosphazene<sup>2a</sup> (Phosponitrilic Chloride Trimer) with Aromatic Dihydroxy, Dithiol, and Diamino Compounds

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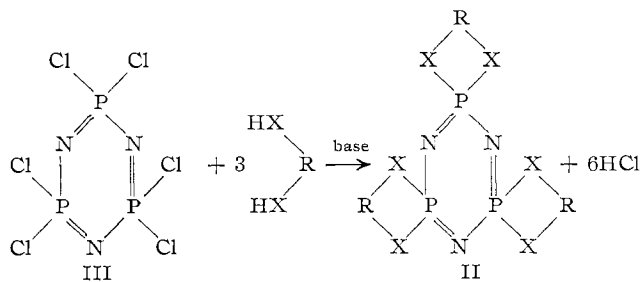
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Hexachlorocyclotriphosphazene, (NPCl<sub>2</sub>)<sub>3</sub>, reacted with 2,3-dihydroxynaphthalene, with 2,2'-dihydroxybiphenyl, with toluene-3,4-dithiol, and with *o*-phenylenediamine, in the presence of base, to yield, respectively, tris(naphthyl-2,3-dioxy)cyclotriphosphazene, tris(diphenyl-2,2'-dioxy)cyclotriphosphazene, tris(1-methylphenyl-3,4-dithio)cyclotriphosphazene, and tris(*o*-phenylenediamino)cyclotriphosphazene. When the reactant stoichiometry for the *o*-phenylenediamine reaction was changed, 1,1-*o*-phenylenediamino-3,3,5,5-tetrachlorocyclotriphosphazene was also obtained. The products were characterized by analytical, infrared, ultraviolet, and nmr methods, and the polymerization, inclusion, and polarographic behavior of specific compounds were examined. No evidence was found for interaction of the  $\pi$  electrons of the cyclophosphazene system with the lone-pair or  $\pi$  electrons of the side groups.

### Results and Discussion

We have recently reported the synthesis, characterization, polymerization, inclusion behavior, and preliminary crystal structure of tris(*o*-phenylenedioxy)cyclotriphosphazene (I) [tris(*o*-phenylenedioxy)phosponitrile trimer].<sup>3-5</sup> The present communication describes an extension of this work to other trimeric phosphazene compounds which contain bulky, cyclic groups attached to the phosphorus atoms. In particular, the approach was designed to provide information about the diversity of the side-group cyclization reaction, about the ease of polymerization of the cyclic trimers, and about the ability of the compounds to form molecular inclusion adducts.

**Syntheses.**—The general reaction scheme used for the preparation of the cyclized compounds (II) was similar to that employed for the preparation of I.<sup>3,4</sup> It involved the reaction of hexachlorocyclotriphosphazene (III) with an aromatic *ortho*-difunctional phenol, thiophenol, or amine, in the presence of a base.



(1) Part IV: H. R. Allcock, P. S. Forgiione, and K. J. Valan, *J. Org. Chem.*, **30**, 947 (1965).

(2) (a) The reasons for use of a "phosphazene" rather than a "phosponitrile" or "hydroazaphosphorine" nomenclature for these compounds has been discussed by R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962). The present notation system, in which numbering is started at the heavier heteroatom (in this case phosphorus), contrasts with the approach favored by the above authors. (b) Author to whom correspondence and reprint requests should be addressed at the Department of Chemistry, The Pennsylvania State University, University Park, Pa.

(3) H. R. Allcock, *J. Am. Chem. Soc.*, **85**, 4050 (1963).

(4) H. R. Allcock, *ibid.*, **86**, 2591 (1964).

(5) H. R. Allcock and L. A. Siegel, *ibid.*, **86**, 5140 (1964).

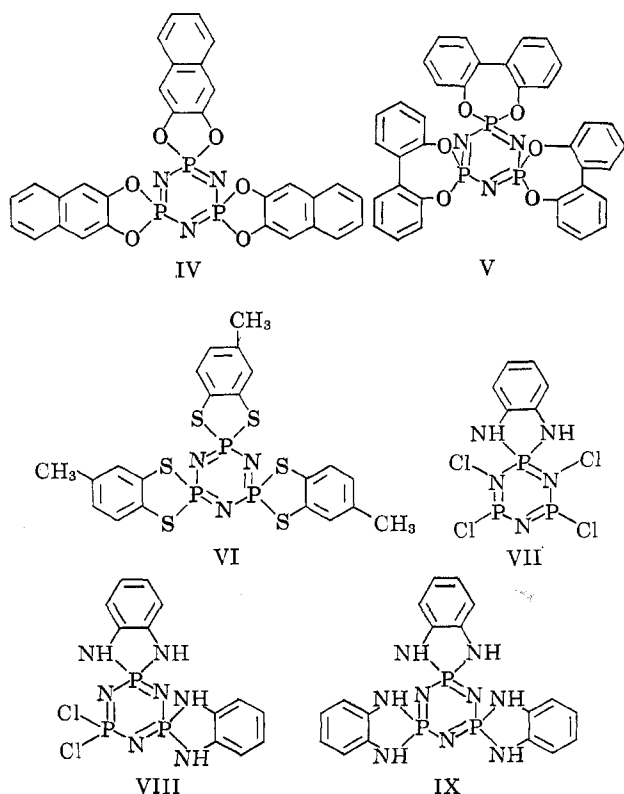
(where R is aromatic and X is O, S, or NH). When *o*-phenylenediamine was used as a reagent, partially substituted phosphazene derivatives were prepared by reducing the ratio of amine to phosphazene below 3:1.

Accordingly, hexachlorocyclotriphosphazene (III) was treated with three molar equivalents of 2,3-dihydroxynaphthalene, 2,2'-dihydroxybiphenyl, toluene-3,4-dithiol, or with one, two, or three molar equivalents of *o*-phenylenediamine, in the presence of solvent and base, to yield, respectively, tris(naphthyl-2,3-dioxy)cyclotriphosphazene (IV), tris(diphenyl-2,2'-dioxy)cyclotriphosphazene (V), tris(1-methylphenyl-3,4-dithio)cyclotriphosphazene (VI), 1,1-*o*-phenylenediamino-3,3,5,5-tetrachlorocyclotriphosphazene (VII), 1,1,3,3-bis(*o*-phenylenediamino)-5,5-dichlorocyclotriphosphazene (VIII), and tris(*o*-phenylenediamino)cyclotriphosphazene (IX).

Of the three *o*-phenylenediamino derivatives (VII, VIII, and IX), the bis(*o*-phenylenediamino) compound (VIII) proved to be the most difficult to isolate in the pure state owing to the ease of intermolecular dehydrohalogenation and cross-linking. The mono-*o*-phenylenediamino derivative was reported previously by Bode, Butow, and Lienau,<sup>6</sup> who treated one molar equivalent of III with two molar equivalents of *o*-phenylenediamine. There was no evidence with any of these reactions that cyclization occurred through *meta*-phosphorus atoms. The structural proof for these derivatives is discussed in the following sections.

**Spectral and Polarographic Data.**—The principal infrared bands for IV to VII and IX as Nujol mulls were as follows (in cm<sup>-1</sup>): IV, 1275 (O—C), 1210 (P=N), 845, 870 s (P—O—Ar), 758 (aryl); V, 1226 multiple band (O—C), 1170 (P=N), 885 (P—O—Ar), 750 doublet, 782 doublet (aryl); VI, 1170 (P=N), 810, 865–880 w (aryl); VII, 3240, 3330 (N—H), 1280 (N—C), 1190 (P=N), 840, 860 (P—N—Ar), 745 (aryl); IX, 3250 (N—H), 1280 (N—C), 1175 (P=N), 820 (P—N—Ar), 738 (aryl). An important feature of

(6) H. Bode, K. Butow, and G. Lienau, *Chem. Ber.*, **81**, 547 (1948).



the spectra concerns the position of the phosphorus-nitrogen stretching peak (asymmetrical ring stretching mode) in the  $1200\text{-cm}^{-1}$  region. In general, electron withdrawal by the side groups should raise the frequency of this band owing partly to the bond strengthening which results from the greater  $d\pi\text{-}p\pi$  character in these circumstances.<sup>7,8</sup> The data are consistent with the view that *o*-phenylenediamino or *o*-dithioaryl groups are less electron withdrawing than chloro or *o*-dioxyaryl in this environment. The spectrum of the mono-*o*-phenylenediamino derivative (VII) provided evidence for hydrogen bonding in the solid state. The spectrum of the solid showed two distinct peaks, due to N-H stretching, at  $3240$  and  $3330\text{ cm}^{-1}$ . A spectrum of a benzene solution of VII showed only one N-H peak at  $3400\text{ cm}^{-1}$ , and a spectrum of VII in tetrahydrofuran showed only one peak at  $3200\text{ cm}^{-1}$ . The  $3330\text{-}$  and  $3400\text{-cm}^{-1}$  peaks were attributed to hydrogen-bonded, N-H stretching, and the  $3200\text{-}$  and  $3240\text{-cm}^{-1}$  peaks to freer N-H stretching. Both hydrogen-bonded and freer N-H groups appear to coexist in the crystalline state.

The ultraviolet absorption peaks of IV, V, VI, VII, and IX in acetonitrile were as follows (in  $m\mu$  with  $\log \epsilon$  values in parentheses): IV, 222 (5.26), 254 (4.07), 264 (4.16), 273 (4.16), 284 (3.98), 297 (3.38), 303 (3.55), 309 (3.47), 317 (3.73); V, 244 (4.68), 269 sh (3.88), 277 sh (3.76); VI, 231 (4.99), 278 (4.46), 288 (4.59); VII, 284 (3.69), 290 sh (3.62); IX, 277 sh (4.21), 290 (4.12). These spectra correspond closely to those of 2,3-dimethoxynaphthalene, 2,2'-dimethoxybiphenyl<sup>9</sup> and

2,7-dihydro-3,4,5,6-dibenzoxepin,<sup>10</sup> 3,4-dithiomethyltoluene, *N,N'*-dimethyl-*o*-phenylenediamine,<sup>11,12</sup> and *o*-phenylenediamine. In general, the ultraviolet spectra indicate that there is little if any resonance interaction between the side groups or between the side groups and the phosphazene ring system. In no case is there a noticeable lengthening of the absorption wavelengths due to an increased delocalization.<sup>13</sup> Such shifts as are apparent involve a change to shorter wavelengths in moving from the side-group analog to the cyclized phosphazene derivative, and this can be ascribed to a reduced aromaticity of the aryl side units which accompanies steric strain or twisting in the oxygen-, nitrogen-, or sulfur-containing rings. The lack of resonance interaction between the side groups and the phosphazene ring suggests that the phosphazene  $\pi$  system is only poorly delocalized.

The nmr data for several of these compounds could not be obtained because of their low solubility in suitable solvents. The following  $P^{31}$  peaks were recorded (values in ppm relative to triethyl phosphate, in solvent specified in parentheses):  $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$ ,  $-9.0$  or  $-10.0$  (dimethylformamide or benzene at  $100^\circ$ ); I,  $-11.8$  (dimethylformamide at  $100^\circ$ ); VII,  $-20$  (tetrahydrofuran); IX,  $-23$  (xylene). The fact that a one-peak spectrum was obtained for VII is unusual. Proton nmr spectra were used to confirm the structures of VI, VII, and IX. The spectrum of the tris(dithiotolyl) derivative (VI) showed aromatic protons and methyl protons at  $\tau$  7.72, with intensities in the ratio of 1:1. The aromatic pattern could be rationalized in terms of 1,2,4-substitution. The spectrum of the mono-*o*-phenylenediamino derivative (VII) was consistent with the expected structure. The aromatic protons were all close to a single peak at  $\tau$  3.31, and the N-H proton peak at  $\tau$  2.01 was broad and showed two lines which probably represent coupling with the  $P^{31}$  ( $J = 14.6$  cps). The NH:aromatic proton ratio was 11.21:24.06. Tris(*o*-phenylenediamino)cyclotriphosphazene (IX) showed a one-peak aromatic proton spectrum in deuterioacetone at  $\tau$  3.48.

The possibility that stable radical-anion or anion species might be formed from heteroaromatic ring systems has been considered by other authors,<sup>14</sup> who attempted, unsuccessfully, to prepare alkali metal adducts of an arylphosphazene ring system. The 2,3-dioxy-naphthyl derivative (IV) appeared to be a particularly suitable compound to examine in this respect since the presence of three naphthyl groups might be expected to exert a stabilizing influence on any reduced species if resonance interactions can be transmitted through

(7) N. L. Paddock, *Quart. Rev. (London)*, **18**, 168 (1964).

(8) D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962).

(9) B. Williamson and W. H. Rodebush, *J. Am. Chem. Soc.*, **63**, 3018 (1941).

(10) G. H. Beaven, D. M. Hall, M. S. Leslie, and E. E. Turner, *J. Chem. Soc.*, 854 (1952).

(11) R. C. Elderfield and V. B. Meyer, *J. Am. Chem. Soc.*, **76**, 1887 (1954).

(12) P. Grammaticakis, *Bull. Soc. Chim. France*, [5] **18**, 534 (1951).

(13) A similar result was found for  $[\text{NP}(\text{C}_6\text{H}_5)_2]_3$  ( $\lambda_{\text{max}}$  260  $m\mu$ ) by R. A. Shaw and F. B. G. Wells, *Chem. Ind. (London)*, 1189 (1960).

(14) D. Chapman, S. H. Glarum, and A. G. Massey, *J. Chem. Soc.*, 3140 (1963).

the molecule. Two one-electron reduction processes were detected at  $E_{1/2} = -2.1$  and  $-2.3$  v. A possible third reduction was obscured by the background current. No reoxidation of the reduced products was detected at a mercury-drop electrode. Since the lifetime of the reduction product or products produced at  $E_{1/2} = -2.1$  v was less than 0.1 sec, it was concluded that the reduced species are unstable and undergo rapid cleavage reactions. Compound IV could not be oxidized at platinum.

**Polymerization Behavior.**—The ability of compound I to polymerize by phosphazene ring cleavage when heated above  $250^\circ$  was reported previously, and this behavior was ascribed to the existence of side-group steric strain.<sup>15</sup> However, it was found that the 2,3-dioxynaphthyl compound (IV) and the 3,4-dithiotolyl compound (VI) underwent side-group rearrangement rather than phosphazene ring cleavage when heated at  $330$  and  $250^\circ$ , respectively. Both tris(*o*-phenylenediamino)cyclotriphosphazene (IX) and tris(2,2'-dioxydiphenyl)cyclotriphosphazene (V) were resistant to polymerization or decomposition at temperatures up to  $300^\circ$ . In the latter case, steric widening of the O–P–O angle, as in  $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$ , may serve to stabilize the cyclic trimeric structure relative to the larger cyclic or open-chain homologs.

**Molecular Inclusion Adducts.**—The unusual molecular inclusion behavior of I has been reported previously.<sup>5</sup> X-Ray diffraction studies indicated that the guest molecules occupy channels between the benzo-dioxiphosphole side groups.<sup>5,15a</sup> Since the inclusion behavior was attributed to the "paddle wheel" like structure of the molecule, it appeared possible that related phosphazene derivatives might behave similarly.

Of the phosphazene derivatives described here, only the dioxynaphthyl compound (IV) has been unambiguously shown to behave in a similar way. In the guest-free state, IV exists in a crystalline structure which is of a lower symmetry than hexagonal.<sup>16</sup> When recrystallized from benzene, the compound forms hexagonal crystals which retain appreciable amounts of benzene. A single-crystal X-ray analysis of the hexagonal form indicated that the *a*-axis parameter was 15.75 Å and the *c*-axis, 10.19 Å. Thus, although the *c*-axis distance is very close to the value found for I (10.08 Å), which indicates that the separation between the layers of phosphazene rings is similar, the *a*-axis distance for IV was appreciably larger than for I (11.73 Å). This is consistent with the crystal structure proposed for I,<sup>5,15a</sup> in which the plane of the host molecule lies along the *a*-axis translations. The increased *a*-axis value for IV thus represents an increased radial diameter associated with the naphthyl groups. The measured density of the crystals of IV was 1.341 g/cm<sup>3</sup>. If, therefore,

there are two parent molecules in each unit cell, about seven benzene molecules are required to conform to the expected molecular weight of IV. Removal of benzene from a recrystallized adduct by heating under vacuum at  $80$ – $100^\circ$  for 3 days indicated that the adduct components were in the ratio of approximately one molecule of IV to two molecules of benzene.

The molar ratio of benzene to IV is more than four times higher than the ratio of benzene to I. This undoubtedly represents the larger cross section of the channels present in hexagonal crystals of IV, which in turn is due to the larger dimensions of the naphthyl compared with the phenyl side groups. The fact that the channels in IV must be wider than those in I is also consistent with the observation that crystalline benzene adducts of IV lose benzene slowly on standing at  $25^\circ$  in the atmosphere and that comparatively mild conditions are required to remove all the guest component under vacuum. Permanent *spontaneous* benzene absorption (by mixing of the components) and crystal rearrangement does not appear to take place with IV. X-Ray powder evidence was obtained, however, that treatment of pure IV with benzene induced a crystal structure change to hexagonal but that, as soon as the adduct was dried in the atmosphere, the included benzene was lost and the crystal structure reverted to its original form. Clearly, the adducts formed between small molecules such as benzene and IV are less stable than those formed by I, but the mechanisms of adduct formation in the two cases appear to be similar.

The tris(*o*-phenylenediamino) derivative (IX) was purified by recrystallization from methyl ethyl ketone. The crystals obtained were apparently not of hexagonal structure, a fourfold symmetry being apparent. After prolonged evacuation at  $80^\circ$  (0.1 mm), the crystals were found to have undergone a crystallographic change, and an appreciable weight loss had occurred. This process could be reversed by addition of methyl ethyl ketone followed by air drying. The presence of methyl ethyl ketone within the crystal structure was confirmed by the infrared spectrum of the solid. The weight-loss and -gain experiments indicated that the molar ratio of IX to methyl ethyl ketone in the adduct was 1:1.8. The possibility that hydrogen bonding is partly responsible for the formation of adducts between IX and ketone cannot be excluded.

No molecular inclusion adducts were detected with the other derivatives, however. It appears likely that the presence of methyl substituents in VI causes some crystal disorder owing to the presence of two isomers. The cavities formed between molecules of V in the crystalline state are probably too large to permit guest molecules to be retained. It is clear from these results that a fairly critical molecular geometry is required before cyclotriphosphazenes can participate in the formation of molecular inclusion adducts. The electronic structure of the cyclophosphazene system apparently has little or no bearing on the inclusion behavior, and the ring serves mainly as a rigid base for the orientation of the side groups.

(15) (a) X-Ray diffraction results show that the O–P–O angle in I is  $97^\circ$ : L. A. Siegel and J. H. van den Hende, private communication. (b) Compare this with the value of  $102^\circ$  reported for  $(\text{NPCl}_2)_3$ : A. Wilson and D. F. Carroll, *J. Chem. Soc.*, 2548 (1960).

(16) Guest-free crystals which were of sufficient size for single-crystal work could not be obtained by sublimation.

TABLE I  
 ANALYTICAL DATA

		C	H	Cl	N	P	S	Mol wt
IV	Calcd for C <sub>30</sub> H <sub>18</sub> O <sub>6</sub> N <sub>3</sub> P <sub>3</sub>	59.11	2.96	...	6.89	15.27	...	612
	Found	58.79	3.28	0	7.09	15.26	...	612 <sup>a</sup>
V	Calcd for C <sub>36</sub> H <sub>24</sub> O <sub>6</sub> N <sub>3</sub> P <sub>3</sub>	62.79	3.49	...	6.11	13.53	...	687
	Found	62.96	3.71	0	6.06	13.61	...	687 <sup>a</sup>
VI	Calcd for C <sub>21</sub> H <sub>18</sub> N <sub>3</sub> P <sub>3</sub> S <sub>6</sub>	42.21	3.02	...	7.03	15.58	32.16	579
	Found	42.12	3.28	0	7.03	15.53	31.71	586 (50.7) <sup>b</sup>
VII	Calcd for C <sub>6</sub> H <sub>5</sub> Cl <sub>4</sub> N <sub>3</sub> P <sub>3</sub>	18.79	1.57	37.1	18.26	24.25	...	383
	Found	18.71	2.36	36.69	18.08	24.37	...	383, <sup>a</sup> 394 <sup>b</sup>
IX	Calcd for C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> P <sub>3</sub>	47.68	3.98	...	27.81	20.53	...	453
	Found	47.95	4.36	0	27.88	20.19	...	c

<sup>a</sup> By X-ray unit cell measurement. <sup>b</sup> By vapor pressure lowering in benzene. <sup>c</sup> Molecular weight data could not be obtained by X-ray analysis because of the clathration behavior (see text). In acetone at 30, 40, and 50° vapor pressure molecular weight values of 941, 777, and 768, respectively, were found. This behavior was ascribed to strong association through hydrogen bonds.

### Experimental Section<sup>17</sup>

**Materials.**—Hexachlorocyclotriphosphazene (III) (Hooker Chemical Corp.) was recrystallized from *n*-heptane to give material of mp 114°. 2,3-Dihydroxynaphthalene (Aldrich) and toluene-3,4-dithiol (Eastman) were used as received. 2,2'-Dihydroxybiphenyl was dried at 25° (0.5 mm.) for 2 hr before use. *o*-Phenylenediamine (Eastman practical grade) was purified by recrystallization from a chloroform-ethyl acetate mixture. Triethylamine (Eastman) was either used as received or dried over anhydrous magnesium sulfate. Tetrahydrofuran (Fisher reagent grade) and benzene (Baker and Adamson reagent grade) were dried over calcium hydride. The sodium carbonate used (Baker and Adamson) was powdered, anhydrous grade material.

**Tris(naphthyl-2,3-dioxy)cyclotriphosphazene (IV).**<sup>18</sup>—A mixture of hexachlorocyclotriphosphazene (50 g, 0.144 mole), 2,3-dihydroxynaphthalene (69.1 g, 0.432 mole), sodium carbonate (91.6 g, 0.864 mole), and tetrahydrofuran (500 ml) was stirred and refluxed for 6 hr and was then stirred at 25° for a further 16 hr. The white precipitate was filtered off, washed with tetrahydrofuran (500 ml) and then with water (5 l.). The residue (55 g, 62% yield) was essentially pure tris(naphthyl-2,3-dioxy)cyclotriphosphazene. Recrystallization from benzene yielded colorless crystals, mp 335–336°, which underwent a visible crystal transformation, accompanied by release of benzene, at 250°. Analytical samples were prepared either by prolonged heating at 100° under vacuum or by sublimation at 350° (0.5 mm).

**Tris(diphenyl-2,2'-dioxy)cyclotriphosphazene (V).**—A mixture of hexachlorocyclotriphosphazene (50 g, 0.144 mole), 2,2'-dihydroxybiphenyl (81.2 g, 0.432 mole), sodium carbonate (91.6 g, 0.864 mole), and tetrahydrofuran (500 ml) was refluxed for a total of 17 hr and was stirred at 25° for a further 40 hr. The white residue was then filtered off and washed with a large excess of water until the washings were no longer basic to litmus. The residue (70.5 g) appeared to consist almost entirely of the required product. A portion was recrystallized from xylene at 200° within a sealed Pyrex tube to give white crystals of tris(diphenyl-2,2'-dioxy)cyclotriphosphazene which did not melt below 300°.

(17) The nmr spectra were measured on a Varian DP60 apparatus with proton spectra determined at 56.4 Mc and P<sup>31</sup> spectra at 16.2 Mc, or on a Varian A60 apparatus. Infrared spectra were recorded using Perkin-Elmer Model 21 and 137 spectrometers, and ultraviolet spectra were measured using a Cary Model 14 automatic recording spectrometer. The polarographic measurements were made on an operational amplifier-based, three-electrode, electronic polarograph. Single-crystal X-ray photographs were obtained with a standard equiinclination Weissenberg camera, and powder patterns were obtained using a 114.6-mm diameter Debye-Scherrer camera. Nickel-filtered Cu K $\alpha$  radiation was employed in both cases. Density measurements for unit cell determinations were measured by a flotation method in aqueous salt solution (for IV) or in organic density columns (for V and VII).

(18) In the earlier synthesis of I, triethylamine or pyridine was used as the hydrohalide acceptor.<sup>34</sup> Triethylamine was also employed as a base in the present work for the synthesis of VI, VII, VIII, and IX. However, in the synthesis of IV and V (and also in the more recent synthesis of I) the use of sodium carbonate for this purpose gave higher yields and cleaner reaction products.

**Tris(1-methylphenyl-3,4-dithio)cyclotriphosphazene (VI).**—A solution of toluene-3,4-dithiol (10 g, 0.064 mole) and triethylamine (12.06 g, 0.119 mole) in tetrahydrofuran (75 ml) was added over 30 min to a stirred solution of hexachlorocyclotriphosphazene (6.96 g, 0.02 mole) in tetrahydrofuran (25 ml). The reaction was exothermic. Tetrahydrofuran (50 ml) was added to maintain the fluidity, and the mixture was stirred at 25° for 3 hr and allowed to stand at the same temperature for a further 2.5 days. The white precipitate was filtered off, washed with tetrahydrofuran (100 ml), and dried under vacuum (18.7 g). This solid was then washed with water (2 l.) to remove triethylamine hydrochloride (15 g). The residue (3.7 g) was recrystallized from toluene and from xylene to yield tris(1-methylphenyl-3,4-dithio)cyclotriphosphazene, mp 255–257°.

**1,1-*o*-Phenylenediamino-3,3,5,5-tetrachlorocyclotriphosphazene (VII).**—A solution of *o*-phenylenediamine (9 g, 0.0833 mole) and triethylamine (16.6 g, 0.166 mole) in tetrahydrofuran (100 ml) was added during 15 min to a refluxing solution of hexachlorocyclotriphosphazene (29 g, 0.0833 mole) in tetrahydrofuran (100 ml). A precipitate formed as the mixture was refluxed for 3 hr. The mixture was then filtered, and the solids were washed with tetrahydrofuran and dried (21.5 g) (theory triethylamine hydrochloride, 23.1 g). The combined filtrates were evaporated to dryness, and the residue was extracted with *n*-hexane in a Soxhlet apparatus. The product which crystallized from *n*-hexane was 1,1-*o*-phenylenediamino-3,3,5,5-tetrachlorocyclotriphosphazene (9.3 g, 29% yield). A melting point value of 325° was obtained by a bracketing technique at nine different temperatures in this range. The melting point could not be determined by a direct conventional method because the compound polymerized in the solid state as the temperature was raised.

**1,1,3,3-Bis(*o*-phenylenediamino)-5,5-dichlorocyclotriphosphazene (VIII).**—A solution of *o*-phenylenediamine (21.6 g, 0.2 mole) and triethylamine (40.4 g, 0.4 mole) in tetrahydrofuran (200 ml) was added over a period of 2 hr to a stirred solution of hexachlorocyclotriphosphazene (34.8 g, 0.1 mole) in tetrahydrofuran (200 ml) at 25°. The mixture was stirred at 25° for a further 2 hr, and the precipitate filtered off (40.4 g of triethylamine hydrochloride). The filtrate was then refluxed for 2 hr and was filtered hot to remove the insoluble triethylamine hydrochloride (14 g). The filtrate was allowed to stand at 25° for 3 days, during which time large, colorless crystals were deposited (10.6 g). Attempts to purify this product, by recrystallization or sublimation, resulted in decomposition. The solid did not melt below 300°. An infrared spectrum of the product was similar to those of VII and IX, and the relative peak heights were intermediate between those of VII and IX. The microanalytical data (C, 43.84; H, 5.50; Cl, 14.24) indicated that appreciable condensation by dehydrohalogenation had occurred.

**Tris(*o*-phenylenediamino)cyclotriphosphazene (IX).**—A solution of *o*-phenylenediamine (32.4 g, 0.3 mole) and triethylamine (60.0 g, 0.6 mole) in tetrahydrofuran (300 ml) was added dropwise to a stirred solution of hexachlorocyclotriphosphazene (34.8 g, 0.1 mole) in tetrahydrofuran (200 ml). The mixture was re-

fluxed for 16 hr and then cooled to 25°. The precipitate was filtered off, washed with tetrahydrofuran, and dried (111.7 g). This material was then washed with water to remove triethylamine hydrochloride (78.9 g; theory, 82 g). The residue was crude IX (32.8 g, 72.3%). This material was recrystallized from aqueous acetone or methyl ethyl ketone to yield white or pale yellow needles of tris(*o*-phenylenediamino)cyclotriphosphazene. The compound did not melt below 300° and could not be sublimed at 300° (0.5 mm). It was insoluble in hexane, benzene, toluene, dioxane, carbon tetrachloride, and water. It was sparingly soluble in acetone, acetonitrile, or methyl ethyl ketone.

**Analyses.**—Analytical data for compounds IV to VII and IX are shown in Table I.

**Polymerizations.**—Polymerizations were attempted by heating samples of each compound under vacuum at temperatures up to 300° for between 4 and 8 hr. Any changes were followed by

infrared spectra and melting point. The weight-average molecular weight value of the linear macrocyclic polymer produced from I (after removal of trimer at 300° (0.05 mm)) was found to be 13,000 by light-scattering measurements in dimethylformamide. The brittle polymer produced from IV after 5 hr at 300° under vacuum was too insoluble for the molecular weight to be determined. Infrared spectra suggested that rearrangement of both the phosphazene and naphthyldioxaphosphole units had occurred.

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## Metal Ion-Aromatic Complexes. II. The Crystal Structure of the 1:1 Silver Nitrate-Pyrazine Complex

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The crystal structure of the 1:1 silver nitrate-pyrazine complex has been determined by three-dimensional, single-crystal X-ray diffraction techniques. The structure consists of almost planar-kinked chains of the type  $[-Ag-NC_4H_4N-]_z$  with Ag-N distances of  $2.213 \pm 0.014$  Å and N-Ag-N' angles of  $159.2 \pm 0.9^\circ$ . Next nearest neighbors of Ag(I) are two oxygens of a nitrate group at  $2.720 \pm 0.021$  Å and two other nitrate oxygens at  $2.943 \pm 0.017$  Å. The chains are held together by weak or van der Waals interactions. The crystals are all inherently twinned.

### Introduction

Covalently bonded Ag(I) is most commonly found with a coordination number of two or four with linear and tetrahedral geometry, respectively. The best known examples with coordination number two are linear  $Ag(NH_3)_2^+$  and  $Ag(CN)_2^-$ .<sup>3a</sup> An example of tetrahedral fourfold coordination is  $Ag[SC(CH_3)-NH_2]_4Cl$ .<sup>4</sup> However, Ag(I) also forms crystalline organic complexes with completely different geometries and bonding from the above. Some of these are:  $Ag^+ \cdot C_6H_6 \cdot ClO_4^-$ ,<sup>5</sup>  $Ag^+ \cdot C_5H_5 \cdot NO_3^-$ ,<sup>6</sup>  $Ag^+ \cdot C_6H_6 \cdot AlCl_4^-$ ,<sup>7</sup> and  $Ag^+ \cdot 3C_4H_8O_2 \cdot ClO_4^-$ .<sup>8</sup> The first three are "π" complexes, and the fourth is an "ionic" complex with octahedral coordination about Ag(I).

The complex  $AgNO_3 \cdot N_2C_4H_4$ <sup>9</sup> recently was prepared, and some of its physical properties were reported. The complex was found to be stable in air and in-

soluble in water—unusual properties for this type of compound.

As part of a continuing structure study of metal ion-aromatic complexes, a crystal structural investigation of this compound was undertaken to determine the stereochemical reasons for its stability as well as to observe the effect of complex formation on the aromatic system.

### Experimental Section

Needle crystals of  $AgNO_3 \cdot N_2C_4H_4$  appropriate for diffraction purposes were grown by the slow cooling of a reaction mixture of pyrazine and silver nitrate in warm water.<sup>9</sup> Precession and Weissenberg photographs taken with Mo K $\alpha$  radiation revealed the crystals to be monoclinic with  $a = 14.21 \pm 0.04$ ,  $b = 6.47 \pm 0.02$ ,  $c = 3.56 \pm 0.01$  Å, and  $\beta = 95^\circ 15' \pm 10'$  (Mo K $\alpha = 0.7107$  Å). The calculated density of  $2.53$  g cm<sup>-3</sup>, based on two formula species per unit cell, is in satisfactory agreement with the experimental value of  $2.56$  g cm<sup>-3</sup> obtained by the flotation method. Systematic absences of  $h = 2n + 1$  for  $h0l$  indicate the probable space group to be Pa or P2/a. The choice between the space groups was established by the X-ray analysis (*vide infra*). A needle crystal of  $0.10 \times 0.15 \times 0.80$  mm dimensions was mounted about the needle axis and used for collecting the intensity data. Since the linear absorption coefficient ( $\mu$ ) for this compound with Mo K $\alpha$  radiation is only  $34$  cm<sup>-1</sup>, no absorption corrections were made.

Equiinclination Weissenberg multiple-film intensity data were collected for  $hk0$ - $hk3$  levels with Zr-filtered Mo K $\alpha$  radiation. In addition,  $h0l$  and  $0kl$  timed exposure precession photographic

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