In the yellow form, they occupy all of the octahedrally coordinated voids between alternate iodine layers, giving a layer structure with respect to the Hg–I primary bonds. These stacking relationships are illustrated in Figure 1 and the first neighbor distances between like and unlike atoms are shown in Table III.

TABLE III

INTERATOMIC NEAREST NEIGHBOR DISTANCES (A) IN RED AND YELLOW MERCURIC IODIDE

Yellow HgI_2		Red HgI_2	
Hg–I	2.615[a]	4Hg–I	2.783
Hg–I	2.620[a]	4I–I	4.142
2Hg–I	3.507	4I–I	4.361
2Hg–I	3.510	4I–I	4.635
I–I	4.017[b]	4Hg–Hg	4.361
2I-I	4.256	4Hg–Hg	6.167
2I–I	4.356	($\sigma \approx 0.003$ A)	
4I–I	4.397		
2I–I	4.702		
I–I	5.208		
I–I	5.235[a]		
2Hg–Hg	4.397		
4Hg–Hg	4.702		
($\sigma \approx 0.006$ A)			

[a] Within the HgI_2 molecule, with I–Hg–I = 178.3°. [b] Between the $(HgI_2)_n$ layers.

A consequence of the alternation of Hg sites between the I layers is a greater distortion from ideal packing, and this is apparent in the interatomic distances. Thus in the yellow form, the 12 first-neighbor I–I distances range from 4.017 to 5.234 A, while in the red form, where the Hg atoms are more uniformly distributed between the iodines, the range is only over 0.5 A. In the HgI_4 tetrahedra of the red form, the bonds are equal by symmetry but the angles are distorted to 103.14 and 112.72°. The Hg–I distances of 2.783 A are 0.02 A longer than the sum of the tetrahedral radii $r[\mathrm{Hg}(4)] = 1.48$ A and $r[\mathrm{I}(4)] = 1.28$ A, recently reported.[13] The HgI_6 octahedra of the yellow form are much more distorted with two short Hg–I distances of 2.617 A and four long distances of 3.508 A, the internal angles at the Hg atom varying from 85 to 95°. The structure approaches closely therefore to that of a molecular arrangement of HgI_2 molecules, with Hg–I bonds equal to the sum of the covalent radii, $r[\mathrm{Hg}(2)] = 1.28$ A and $r[\mathrm{I}(2)] = 1.33$ A, and is in agreement with measurements in the vapor phase from electron diffraction studies.[14,15] The I–Hg–I angle is 178.3° with an estimated standard deviation of 0.3°, indicating a small but significant deviation from linearity. The HgI_2 molecules lie parallel to a direction at 1.5° to the [012] axis, *i.e.*, inclined at 45.5° to the [*c*] and in the (200) planes. The Hg–I molecular bonds are indicated by dotted lines in Figure 1. The four long Hg–I distances are about 0.1 A shorter than the sum of the usually accepted van der Waals radii (*i.e.*, 1.50 + 2.15 A). The shortest of the 12 first-neighbor I–I distances is that between the HgI_2 layers and is about 0.3 A less than the van der Waals diameter.

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Some Reactions of Chlorosilazanes[1]

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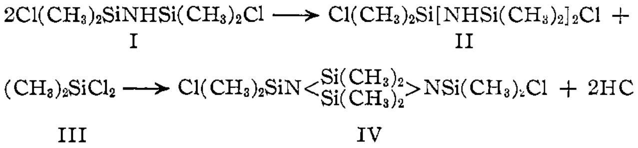
The preparation of 1,3-dichlorotetramethyldisilazane, $Cl(CH_3)_2SiNHSi(CH_3)_2Cl$ (I), has recently been described.[2]

It has been shown that on refluxing a linear or cyclic dimethylpolysilazane with dimethyldichlorosilane, 1,3-dichlorotetramethyldisilazane is obtained.

Further investigation of this reaction revealed that only by refluxing the polysilazane with an excess of dimethyldichlorosilane, 1,3-dichlorotetramethyldisilazane is formed as the favored product, but the formation of 1,3-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (IV) is favored when stoichiometric amounts of reactants are refluxed for several hours. However, 1,3-dichlorotetramethyldisilazane is initially formed also in the latter case. It then disproportionates to yield the unstable compound (II) from which [by reaction with dimethyldichlorosilane (III) previously liberated] 1,3-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (IV) is formed



$$\underset{\mathrm{I}}{2Cl(CH_3)_2SiNHSi(CH_3)_2Cl} \longrightarrow \underset{\mathrm{II}}{Cl(CH_3)_2Si[NHSi(CH_3)_2]_2Cl} + \underset{\mathrm{III}}{(CH_3)_2SiCl_2} \longrightarrow \underset{\mathrm{IV}}{Cl(CH_3)_2SiN{<}\genfrac{}{}{0pt}{}{Si(CH_3)_2}{Si(CH_3)_2}{>}NSi(CH_3)_2Cl} + 2HC$$

The structure of IV has also been confirmed by two other authors,[2a,3] who obtained this material by allowing octamethylcyclotetrasilazane to react with dimethyldichlorosilane or 1,3-dichlorotetramethyldisilazane with sodium bis(trimethylsilyl)amide. Compound II is unstable, as on gas chromatographic analysis it disproportionates upon the column to yield a mixture containing compounds I, II, III, and IV. The formula for 1,5-dichlorohexamethyltrisilazane was assigned to it, since the constant chlorine content of this fraction

[1] A part of this work is taken from a Ph.D. thesis to be submitted by J. Fuchs to the Senate of the Hebrew University.

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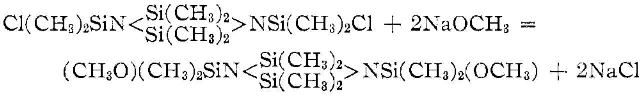
was in accordance with this formula. 1,3-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane (IV) is also obtained on refluxing pure 1,3-dichlorotetramethyldisilazane (I). The reaction scheme can be further substantiated by determining the composition of the reaction mixture during reaction using gas chromatographic techniques. So it could be shown that 1,3-dichlorotetramethyldisilazane is formed initially while the concentrations of the silazane polymer and dimethyldichlorosilane decrease proportionally. After prolonged reflux, compound II is formed and only later 1,3 - bis(dimethylchlorosilyl)cyclotetramethyldisilazane appears. This is also in agreement with the redistribution studies by Van Wazer and Moedritzer,[4] who have shown that, upon equilibration, long-chain halogen-terminated silazanes rearrange in favor of short chain and cyclics.

1,3-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane (IV) reacts with sodium methylate to yield 1,3-bis(methoxydimethylsilyl)tetramethylcyclodisilazane (V)



$$\mathrm{Cl(CH_3)_2SiN{<}\genfrac{}{}{0pt}{}{Si(CH_3)_2}{Si(CH_3)_2}{>}NSi(CH_3)_2Cl + 2NaOCH_3 = (CH_3O)(CH_3)_2SiN{<}\genfrac{}{}{0pt}{}{Si(CH_3)_2}{Si(CH_3)_2}{>}NSi(CH_3)_2(OCH_3) + 2NaCl}$$

V

A further reaction of 1,3-dichlorotetramethyldisilazane (I) is that with antimony trifluoride to yield 1,3-difluorotetramethyldisilazane (VI)

$$\mathrm{Cl(CH_3)_2SiNHSi(CH_3)_2Cl \xrightarrow{SbF_3} F(CH_3)_2SiNHSi(CH_3)_2F}$$

VI

The reaction was carried out at low temperature (acetone–Dry Ice bath) so that cleavage of the silazane bond[5] was kept at a minimum.

It is difficult to obtain compound VI by allowing 1,3-dichlorotetramethyldisilazane (I) to react with ammonium fluoride, as the latter reacts also with the silazane bond.[2] Compound VI has recently been prepared by treating a silazane polymer with an ethereal solution of hydrogen fluoride at a low temperature or with a silicon tetrafluoride amine.[6] 1,3-Dichlorotetramethyldisilazane (I) also reacts with methylamine to yield 1,5-dimethyloctamethylcyclotetrasilazane (VII).

$$\mathrm{2Cl(CH_3)_2SiNHSi(CH_3)_2Cl + 6CH_3NH_2 = CH_3N[Si(CH_3)_2NHSi(CH_3)_2]_2NCH_3 + 4CH_3NH_2\cdot HCl}$$

VII

Compound VII has also been prepared by Wannagat[2a] by allowing 1,3-dichloropentamethyldisilazane to react with ammonia. It is known that dimethyldichlorosilane treated with methylamine yields the disubstituted compounds bis(methylamino)dimethylsilane and 1,3-bis(methylamino)pentamethyldisilazane, which are sufficiently stable to be distilled;[7,8] on cyclization preferably nonamethylcyclotrisilazane is formed[9] (yield, 87–93%). However, 1,3-dichlorotetramethyldisilazane, treated with methylamine, readily forms the cyclic compound (VII). Under the reaction conditions used, 1,3-bis(methylamino)tetramethyldisilazane was not isolated.

A further reaction requiring mention is that of hexamethyldisilazane with methyltrichlorosilane, where 1,1,3,3-tetrachlorodimethyldisilazane (VIII) is obtained.

$$\mathrm{(CH_3)_3SiNHSi(CH_3)_3 + 2CH_3SiCl_3 \longrightarrow Cl_2(CH_3)SiNHSi(CH_3)Cl_2 + 2(CH_3)_3SiCl}$$

VIII

As with the reaction between hexamethyldisilazane and dimethyldichlorosilane,[2b] here, too, reaction proceeds only in the presence of a catalyst such as aluminum chloride. Compound VIII is hydrolytically highly unstable and reacts violently with water or alcohol.

Experimental Section[10,11]

Preparation of 1,3-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane.—A mixture of 18.0 g (0.08 mole) of hexamethylcyclotrisilazane and 15.50 g (0.12 mole) of dimethyldichlorosilane was heated to 150° for 24 hr. On cooling, the reaction mixture become solid. On distillation, there was collected 24.70 g (0.07 mole) of 1,3-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, bp 125° (40 mm), mp 62°, yield 78%. *Anal.* Calcd for $\mathrm{Cl(CH_3)_2SiN[Si(CH_3)_2]_2NSi(CH_3)_2Cl}$: C, 29.00; H, 7.25; N, 8.46; Cl, 21.45; Si, 33.81. Found: C, 27.66; H, 7.83; N, 8.27; Cl, 20.63.

The compound was tested by its ^{1}H nmr spectrum (δ 0.34 ppm in $\mathrm{CCl_4}$, room temperature). A further series of experiments was carried out under similar conditions allowing hexamethylcyclotrisilazane, octamethylcyclotetrasilazane, and higher linear silazane polymers to react with dimethyldichlorosilane, using also nonstoichiometric quantities. After completion of reaction, the mixture always contained 1,3-bis(chlorodimethylsilyl)tetramethylcyclodisilazane. If a catalytic amount (200–300 mg) of anhydrous aluminum chloride was added, reaction time was considerably reduced. The same result was obtained by refluxing pure 1,3-dichlorotetramethyldisilazane. At a bath temperature of 140° with $\mathrm{AlCl_3}$ as a catalyst the yield was 30% after 3 hr and ~60% after 6 hr.

Reaction of 1,3-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane with Sodium Methylate.[12]—A solution of 1,3-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (10.00 g, 0.03 mole) in 50 ml of dry ether was well stirred and cooled in an ice bath. Sodium methylate (3.2 g, 0.05 mole) was added slowly. The mixture was then left for 1 hr and finally distilled under vacuum. There was collected 7.0 g (0.02 mole) of 1,3-bis(methoxydimethylsilyl)tetramthylcyclodisilazane (yield 40%, bp 118° (15 mm), $n^{20}\mathrm{D}$ 1.434, d^{25} 0.943 g/ml). *Anal.* Calcd for $\mathrm{(CH_3O)(CH_3)_2SiN[Si(CH_3)_2]_2NSi(CH_3)_2(OCH_3)}$: C, 37.28; H, 9.32; N, 8.71; Si, 34.78. Found: C, 37.70; H, 9.14; N, 8.69; Si, 33.24.

Reaction of 1,3-Dichlorotetramethyldisilazane with Antimony Trifluoride.—A solution of 25.00 g (0.12 mole) of 1,3-dichlorotetramethyldisilazane in 70 ml of dry ether was well stirred and cooled in an acetone–Dry Ice bath. After slow addition of antimony trifluoride (15.50 g, 0.08 mole), the reaction mixture was kept in the cooling bath for 1 hr more and was then allowed to reach room temperature. The reaction product was then distilled

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(10) Analytical samples given were obtained by preparative gas chromatography using a glass column (15 ft × 3/8 in.; packing: 30% silicone SE 30 on 60–80 Chromosorb P).

(11) Part of the analytical results given for C, H, and N were carried out by A. Bernhard, Microanalytical Laboratory, West Germany; other analyses were carried out in our own laboratories.

(12) Prepared by titrating sodium in liquid ammonia with methanol according to J. Chablay, *Compt. Rend.*, **140**, 1340 (1905).

off under high vacuum, collected in a trap cooled with liquid air, and then redistilled. 1,3-Difluorotetramethyldisilazane (9.70 g, 0.057 mole), bp 118° (692 mm) was obtained, yield 47.5%. The compound is hydrolytically unstable. *Anal.* Calcd for $F(CH_3)_2SiNHSi(CH_3)_2F$: C, 28.40; H, 7.69; N, 8.28; Si, 33.4; F, 22.49. Found: C, 28.62; H, 7.86; N, 8.21; Si, 30.0; F, 22.32.

Preparation of 1,1,3,3-Tetrachlorodimethyldisilazane.—Hexamethyldisilazane (20.00 g, 0.12 mole) was mixed with 90.0 g (0.6 mole) of methyltrichlorosilane and a catalytic amount ($\sim$200 mg) of anhydrous aluminum chloride was added. The mixture was refluxed for 2 hr and immediately distilled under high vacuum. The fractions were collected by cooling with liquid air. There was obtained 19.0 g (0.78 mole) of 1,1,3,3-tetrachlorodimethyldisilazane, bp 42° (0.1 mm), yield 65%. *Anal.* Calcd for $Cl_2(CH_3)SiNHSiCl_2(CH_3)$: C, 9.83; H, 2.92; N, 5.76; Cl, 58.43; Si, 23.04. Found: C, 10.12; H, 3.11; N, 5.70; Cl, 59.1; Si, 21.7. The compound is hydrolytically highly unstable.

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A Phosphorus-31 Nuclear Magnetic Resonance Study on the Phosphorus–Iodine System

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A study of the reaction of white phosphorus and iodine was reported[1] in 1940; however, since that time there have been no further attempts to define this system. Wyllie, Ritchie, and Ludlam proposed a mechanism whereby P_2I_4 was obtained from its elements, *via* several iodide intermediates without breaking and re-forming the P–P bond. This mechanism has been extensively referred to as evidence for the existence of iodides other than the tetraiodide and triiodide, which have been isolated in their pure state.

The present report summarizes ^{31}P nuclear magnetic resonance and spectrophotometric evidence that the formation of P_2I_4 from white phosphorus and iodine in the presence of greater than stoichiometric amounts of phosphorus does not take place as previously described.[1] We have shown that all of the P–P bonds are broken when the reaction is carried out in carbon disulfide or carbon tetrachloride at 25°. The initial reaction is rapid, proceeding directly to PI_3, which undergoes a slower reaction with the excess phosphorus to form P_2I_4.

Also, the phosphorus–iodine system is very labile, and evidence is presented for the existence of equilibria in solution.

Experimental Section

Reagents.—Diphosphorus tetraiodide and phosphorus triiodide were prepared in CS_2 from reagent grade iodine and white phosphorus, according to the method of Germann and Traxler.[2] The elemental phosphorus was purified by treatment with dilute HNO_3 at 60°. Upon cooling, the solid was washed with distilled water, absolute methanol, and dry carbon tetrachloride. The CS_2 and CCl_4 solvents were reagent and spectroscopic grade chemicals, respectively. They were dried, distilled, and stored over P_2O_5. Spectroscopic grade cyclohexane was dried over P_2O_5 and used without additional purification. Normal precautions were observed to exclude air and moisture from all reactions.

^{31}P Nmr.—The ^{31}P nmr spectra were obtained with a Varian high-resolution spectrometer operating at 24.288 Mc. Chemical shifts are reported in CS_2 and are relative to 85% H_3PO_4 as an external reference. For the kinetic measurements, a known quantity of iodine in CS_2 was added to a blackened, nitrogen-flushed nmr tube. The reaction was initiated by introducing a known amount of P_4 in CS_2 into the nmr tube. Solutions were transferred with syringes in order to avoid contamination by air and moisture. The nmr tube was then agitated before insertion into the probe.

Data for the kinetic experiments were obtained from the areas of the respective PI_3 and P_2I_4 peaks. Thus, each peak was traced on high-quality tracing paper and weighed. Three tracings were obtained on each peak, and the average weight was used. For a given run, all settings in the spectrometer were kept constant and precautions were taken to avoid saturation of the resonance signals. For some concentrations of the reactants, solids separated out of solution. The kinetic data used were obtained prior to the separation of solids.

The ^{31}P nmr chemical shift of P_2I_4 in CS_2 obtained on a sample of P_2I_4 (mp 124–126°) recrystallized from CS_2 was -108 ppm in contrast to the reported[3] value of -170 ppm. A similar value for the chemical shift of P_2I_4 in CS_2 at 25° was obtained in an independent investigation.[4] The earlier reported value is apparently in error, probably as a result of contamination by PI_3, for the PI_3 chemical shift in CS_2 is -178 ppm.

Spectrophotometric Measurements.—A Cary Model 14 spectrophotometer was used for all measurements. When pure recrystallized PI_3 is dissolved in cyclohexane, three absorption maxima in the ultraviolet region are apparent. These maxima are 374, 287, and 223 mμ. Moeller and Huheey[5] had assigned the 223-mμ maximum to P_2I_4. This assignment was made without considering the disproportionation of P_2I_4 to PI_3 and P_4 upon dissolution in cyclohexane. The existence of this equilibrium is supported by the fact that identical ultraviolet spectra are obtained on cyclohexane solutions of P_2I_4 and PI_3. Employing a value[6] of 1.54×10^3 for the molar absorptivity in cyclohexane at 374 mμ, values at 287 and 223 mμ are 7.34×10^3 and 1.45×10^4, respectively. The molar absorptivity calculated for solutions made by dissolving recrystallized P_2I_4 in the same solvent are, respectively, 7.13×10^3 and 1.49×10^4. These values were obtained soon after dissolution, thus minimizing interference by iodine. Also ^{31}P nmr results supporting the disproportionation of P_2I_4 are given in the next section of this paper.

Results and Discussion

Evidence for PI_3 as a Reaction Intermediate.—When white phosphorus and iodine react at 25°, PI_3 is the first stable compound that can be observed by ^{31}P nmr. When excess phosphorus is present, the PI_3 then reacts with the latter to form P_2I_4. This sequence of reactions, which can be represented by the equations

$$^{1}/_{2}P_4 + 3I_2 \longrightarrow 2PI_3 \qquad (1)$$

$$2PI_3 + {}^{1}/_{4}P_4 \longrightarrow {}^{3}/_{2}P_2I_4 \qquad (2)$$

is represented graphically in Figure 1. The formation of PI_3 from the reaction of white phosphorus with iodine

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