Structural Effects in Heteroatom Systems. I. The Influence of Steric Effects on Oligomer–Polymer Interconversions in the Phosphazene (Phosphonitrile) Series. A Semiempirical Approach

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The influence of side-group steric repulsions on the relative thermodynamic stability of polymeric phosphazenes and on the relative polymerizability of cyclic phosphazenes is discussed. Increasing dimensions of the side groups should progressively lower the ceiling temperature until polymer can no longer exist as a stable entity. A simple, semiempirical, graphical method is employed for the estimation of the maximum overlap of van der Waals rotational boundaries for common side groups. The calculated polymerization and depolymerization tendencies were found to be reasonably consistent with the limited, qualitative experimental data at present available. The results also suggest that most polyorganophosphazenes should occupy a *cis–trans*-planar conformation.

Introduction

In recent years there has been a considerable growth of interest in the synthesis and chemistry of alternant heteroatom chain polymers such as polyphosphazenes, polysiloxanes, polysilazanes, polyphosphinoboranes, and polyoxymethylenes. In many cases, such polymers can be prepared by polymerization of the appropriate cyclic trimers or tetramers, although the polymers so formed frequently depolymerize to cyclic oligomers at high temperatures. The understanding of such polymerization–depolymerization equilibrations constitutes one of the most important problems in heteroatom chemistry.

In the phosphazene series, in particular, considerable qualitative experimental effort has been devoted to the synthesis of cyclic trimeric (I) and tetrameric (II) derivatives with a view to the ultimate polymerization of these to high polymers (III). Only with a limited number of derivatives (principally where R is halogen) have such equilibration attempts been successful.[2] It is clear that the nature of the side group, R, exerts a profound influence on the ability of a
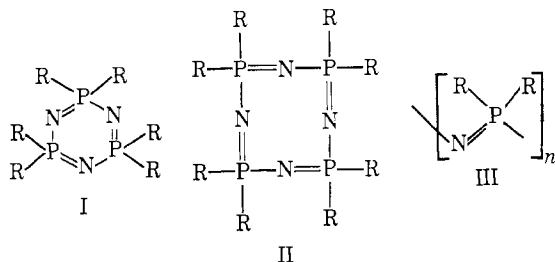
cyclic phosphazene to polymerize and on the position of the polymerization–depolymerization equilibrium.

It has been suggested[3a] that this side-group effect represents a mechanistic influence on the reaction, which is connected with the ease of ionization of the side group from phosphorus, thus facilitating an ionic reaction mechanism. Indeed, conductance experiments have demonstrated that ionization of chloride ion from phosphorus occurs at temperatures where hexachlorocyclotriphosphazene, $(NPCl_2)_3$, undergoes polymerization.[3b] However, at 350° conductance data demonstrated a significant reversible ionization of phenoxy groups from $[NP(OC_6H_5)_2]_3$, although no polymerization was detected at that temperature. Ionization of a side group is thus not the only criterion of polymerizability. It is more reasonable to assume that the ease of ionization at a given temperature determines the rate at which the equilibrium shifts to a more stable state.

It appears that, in a very general way, there is some correlation between the *dimensions* of the side groups and the polymerization or depolymerization behavior of cyclic or polymeric phosphazenes. Small groups appear to favor the polymerization process and large groups favor the depolymerization. In some cases this steric effect may represent a kinetic change, but the predominant influence of the side group appears to be on the thermodynamics of equilibration. In order to demonstrate this conclusion, the relative stabilities of various polymeric phosphazenes will be compared in terms of side group steric overlap parameters.

It must be emphasized that the side group steric influence is only one of several factors which affect ring–polymer equilibria. The effect of bond angles on ring strain and on the statistics of ring closure have been reviewed elsewhere,[4–11] and account must also

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(2) Phosphazene polymerization is discussed in reviews by R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962); C. D. Schmulbach, *Progr. Inorg. Chem.*, **4**, 275 (1962); and N. L. Paddock, *Quart. Rev.* (London), **18**, 168 (1964).

(3) (a) F. G. R. Gimblett, *J. Polymer Sci.*, **60**, 529 (1962); (b) H. R. Allcock and R. J. Best, *Can. J. Chem.*, **42**, 447 (1964).

(4) F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 331 (1950).

(5) F. S. Dainton, T. R. E. Devlin, and P. A. Small, *ibid.*, **51**, 1710 (1955).

(6) P. A. Small, *ibid.*, **51**, 1717 (1955).

(7) F. S. Dainton, K. J. Ivin, and D. A. G. Walmsley, *ibid.*, **56**, 1784 (1960).

(8) F. S. Dainton and K. J. Ivin, *Quart. Rev.* (London), **12**, 61 (1955).

(9) H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, **18**, 1600 (1950).

(10) J. B. Carmichael and J. B. Kinsinger, *J. Polymer Sci.*, **A1**, 2459 (1963).

(11) J. B. Carmichael and J. B. Kinsinger, *Can. J. Chem.*, **42**, 1996 (1964).
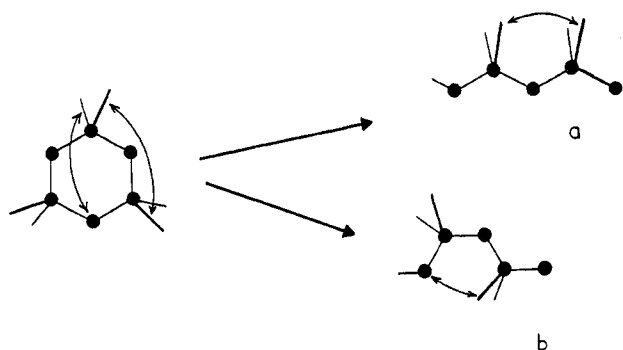
Figure 1.—Change in side-group repulsion on polymerization.

be taken of skeletal bond energies, reaction mechanisms, catalysts, and intramolecular Coulombic interactions. These factors are not considered here. However, the present approach provides a relatively simple method for the assessment of steric effects in hindered polymers, in a way which permits a direct comparison to be made with experimental results.

The Influence of Steric Effects on Equilibration.— In the subsequent qualitative treatment the following premises will be used.

(1) In an equilibrium between cyclic phosphazene oligomers and macrocyclic or linear polymers, steric interference between the side groups or between side groups and chain atoms will change the equilibrium to favor the low molecular weight cyclic products. Steric repulsions in a polymer are nearly always more serious than in the appropriate cyclic trimer or tetramer,[12] and this is true whether the polymer occupies a *trans*-planar, *cis–trans*-planar, or intermediate *gauche* configuration. This is illustrated in Figure 1. These repulsions will be enhanced if the skeletal bond angles are reduced in some way. For instance, steric hindrance between two side groups on the same phosphorus atom should cause the external bond angle between those groups to widen. This in turn should bring about a narrowing of the opposite (skeletal) bond angle owing to a hybridization change.[13,14] Clearly, narrowing of the skeletal angle will favor the formation of small rings rather than larger rings. It will also force the various components

(12) This is not necessarily true for heteroatom systems such as borazenes or silazanes, in which substituents are present on adjacent skeletal atoms, where polymerization of a cyclic oligomer with bulky side groups may actually involve a release of steric strain.

(13) This can be rationalized in terms of a "Thorpe–Ingold effect." Recent analyses of this phenomenon in organic chemistry have been presented by P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 1368 (1961), and in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 117–120 (E. L. Eliel) and pp 460–470 (G. S. Hammond).

(14) In relatively unhindered phosphazenes [*e.g.*, $(NPCl_2)_{3,4,n}$] the ring or chain angle is close to 120° while the external angle between the side units is near 100°: (a) A. Wilson and D. F. Carroll, *J. Chem. Soc.*, 2548 (1960); (b) R. Hazekamp, T. Migchelson, and A. Vos, *Acta Cryst.*, **15**, 539 (1962); (c) A. J. Wagner, A. Vos, J. L. deBoer, and T. Wichertjes, *ibid.*, **16**, A39 (1963); (d) E. Giglio, F. Pompa, and A. Ripamonti, *J. Polymer Sci.*, **59**, 293 (1962). Each angle represents an approximately 10° deviation from the expected sp³ tetrahedral angle. This deviation is almost certainly induced by steric and polar repulsion of the skeletal atoms, accompanied by a hybridization change in the direction of an sp²p structure (opposing angles 120 and 90°). Conversely, if there is a steric repulsion between the two side groups, there should be a tendency for the ring or chain angle to become narrower.
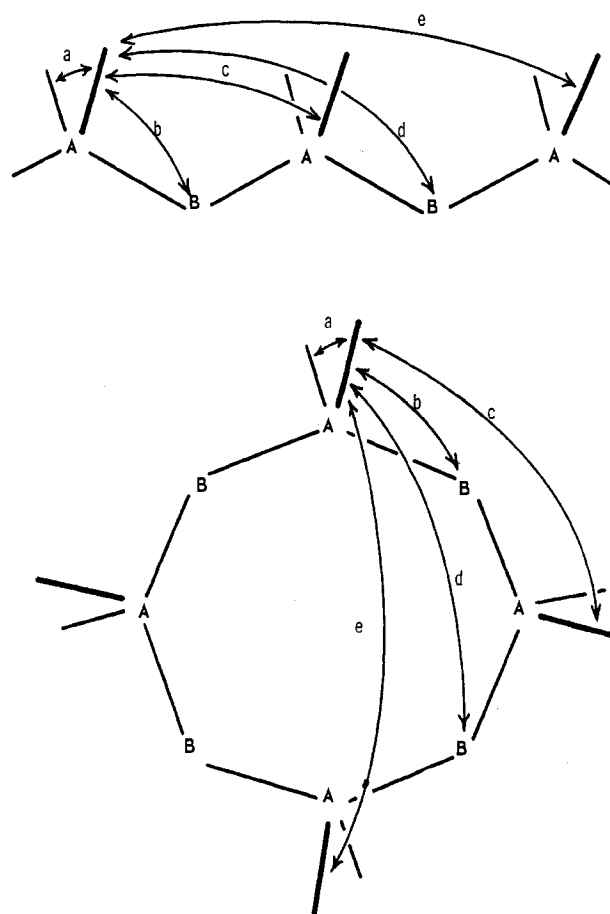

Figure 2.—Steric interactions within a ring or chain.

of the polymer closer together. If appreciable intramolecular crowding is present, small changes in the skeletal angle will have a relatively large effect on the enthalpy of the polymer, but less effect on the trimer or tetramer. An important corollary to this is that, if the angle between the side groups is reduced in some way, there should be a tendency for the internal ring or chain angle to expand, thus favoring the higher cyclic or linear species. This situation would exist if the external bonds were part of a strained cyclic system.

Depolymerization will be favored if the free energy of the polymer is higher than that of the cyclic oligomers. The main influence of steric repulsion is to reduce the rotational entropy of the polymer and to raise the enthalpy of the polymer relative to the low cyclic species. The larger the dimensions of the side groups, therefore, the more the equilibrium should be shifted to the low molecular weight species. Thus, as ΔH for polymerization changes from negative toward zero, the ceiling temperature will be lowered until depolymerization will occur at any temperature.[15]

(2) It follows that the equilibrium will be affected to the largest extent by three particular modes of steric repulsion. These are shown in Figure 2 and are designated as the a-type (1:1), c-type (1:3), and d-type

(15) G. Gee, Chemical Society Special Publication No. 15, International Symposium on Inorganic Polymers, Nottingham, England, July 18–21, 1961, p 67.

(1:4) interactions. Interactions of the b-type (1:2) are relatively unimportant in phosphazene-type polymers since they should be largely independent of the degree of polymerization and of the molecular conformation. The c-type interaction is of primary importance near the *trans*-planar conformation of the chain, and the d interaction is significant near the *cis–trans*-planar conformation. Interactions of the 1:5, 1:6, 1:7, etc., types are inevitable in a random coiled polymer. However, the greater the number of chain atoms between the interacting units, the less is the chance that the combined rotational modes of the intervening segments will lead to repulsions, and the greater is the possibility that the skeletal bonds can rotate independently to relieve the strain. Therefore, a consideration of the a, c, and d repulsions only should provide a basis for determining the influence of the side group on phosphazene equilibration.

(3) A third premise is that the relative degree of steric repulsions between the various components of a polymer can be estimated roughly in terms of overlap area parameters calculated from van der Waals atomic radii and from the rotational (torsional) profiles of polyatomic side groups. This does not mean that interfering groups are assumed to occupy the same space volume but rather that the tendency of two groups to occupy the same volume, by torsional oscillation of the bonds, gives rise to steric repulsion. Overlapping of the rotational van der Waals volumes of multiatomic side groups must reduce the intramolecular degrees of freedom, lower the rotational entropy of the group, and raise the strain enthalpy. The neglect of long-range dipolar forces in this treatment appears to be justified because, for most of the hindered derivatives considered here, the short-range steric repulsions should outweigh the polar interactions.

(4) If steric hindrance within the polymer is small or absent, π-electron or polar influences could exert a relatively large influence on the free energy. However, since phosphorus d orbitals are involved in the π bonding in phosphazenes, the $d\pi$–$p\pi$ overlap should be affected to only a minor extent by changes in ring angle or by ring or chain puckering in the higher homologs, owing to the ease with which alternative d-orbital lobes can be employed. Thus, the skeletal bonds in phosphazenes should be capable of "free" rotation through 360°, and π stabilization of *cis* or *trans* isomeric states should be minimal. However, since the skeletal bonds in phosphazenes undoubtedly have a high $\overset{\ominus}{-}P\overset{\ominus}{-}N-$ polar character, polar attraction of the 1:4 phosphorus and nitrogen atoms should lower the enthalpy of the *cis–trans*-planar configuration (Figure 1b) relative to the *trans*-planar (Figure 1a) and *gauche* configurations. The rotational ground state of an *unhindered* polymer should, therefore, be the *cis–trans*-planar form.

Estimation of Steric Parameters.—A number of methods are available for the estimation of potential functions in terms of Coulombic, London dispersion,

and van der Waals interactions as a function of interatomic distances.[16] For the most part, such empirical calculations give meaningful results only for simple molecules which contain short-chain segments.[17] However, relevant nonbonded interaction functions in polymers have been estimated by DeSantis, Giglio, Liquori, and Ripamonti,[18] who calculated rotational potential functions for a number of organic polymers in terms of both repulsive and attractive interactions as a function of the distance between the interacting atoms. Flory and Mark have shown that the conformation of polyoxymethylene can be explained largely by the dispersion component and to a lesser extent by the Coulombic interactions.[19] In heteroatom systems of the phosphazene type, the situation is likely to be more complicated in view of the greater, and largely unpredictable, charge differences between the skeletal atoms. A much simpler and more empirical approach has, therefore, been used for the present purposes.

Except in a very qualitative way, the nonbonding Coulombic forces have been neglected. This does not necessarily represent a total deviation from reality, since Mason and Kreevoy[20] have shown that van der Waals repulsions account for most of the barrier to rotation in simple molecules. A second assumption which has been made is that the van der Waals repulsions are negligible outside the van der Waals radii distances as determined from intermolecular contact distances.[21] The third and most empirical assumption is that repulsion forces become serious only when the opportunity exists for "collision" of the appropriate van der Waals boundaries. The London dispersion forces are not included because, for most of the derivatives considered, the interactions take place within the sum of the effective van der Waals repulsive radii. Clearly, results based on these assumptions can have a qualitative significance only, but these are of value in explaining or predicting general experimental trends. This approach does permit the influence of multiatomic side groups to be taken into account, a feature which is difficult to incorporate into more refined calculations.

Criteria of Steric Repulsion.—The effective steric boundary of a multiatomic side group is assumed to be the outer surface of the spheroid which is swept out when every bond in the group undergoes a 360° rotation. Rotational boundaries for various common substituent groups were calculated graphically using the following published bond angle, bond length, and van der Waals radii. Bond angles used were as

(16) M. V. Volkenstein, "Configurational Statistics of Polymer Chains," Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 2.

(17) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 10.

(18) P. DeSantis, E. Giglio, A. M. Liquori, and A. Ripamonti, *J. Polymer Sci.*, **A1**, 1383 (1963).

(19) P. J. Flory and J. E. Mark, *Makromol. Chem.*, **75**, 11 (1964).

(20) E. A. Mason and M. M. Kreevoy, *J. Am. Chem. Soc.*, **77**, 5808 (1955).

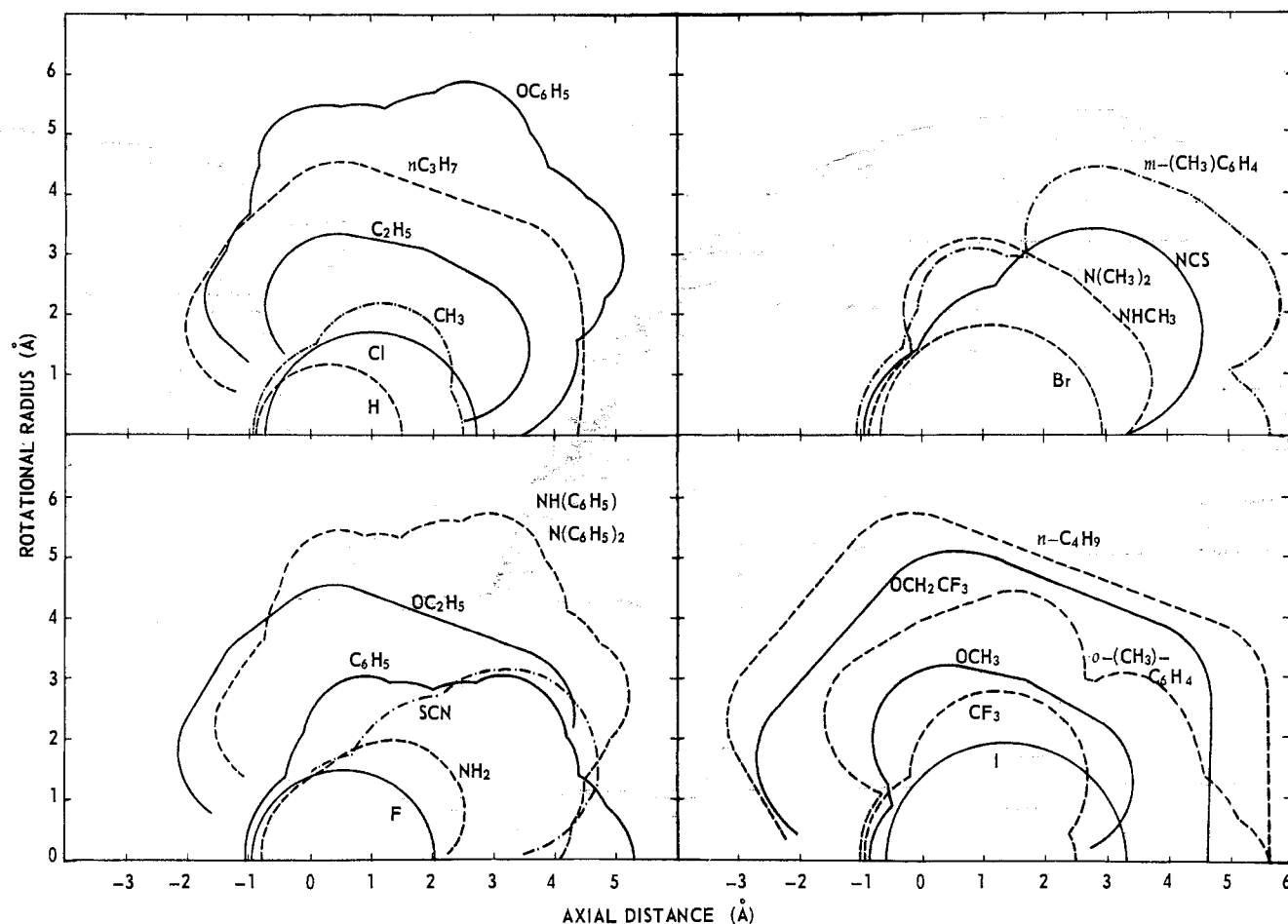(21) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

Figure 3.—Side group rotational boundary profiles.

follows:[22] R—C—R (aliphatic), 109.5°; R—C—R (aromatic), 120°; R—O—R, 112°; H—N—H, 108°; CH_3—N—CH_3, 111°; (C_6H_5)—N—H, 115°; R—S—(CN), 142°; R—N—(CS), 142°; N—C=S, 180°; S—C=N, 180°; N—P—N,[23] 120°; P—N—P,[23] 130°; R—P—R,[23] 103°. The covalent atomic radii were[22] (in A): H, 0.3; F, 0.64; Cl, 0.99; Br, 1.44; I, 1.33; C (aliphatic), 0.77; C (aromatic), 0.67; O, 0.66; N (single), 0.70; N (in N—P),[23] 0.65; N (double), 0.61; N (triple), 0.55; S (single), 1.04; S (double), 0.95; S (triple), 0.88; P (tetrahedral),[23] 0.95. van der Waals radii used were as follows[21] (in A): H (aliphatic), 1.20; H (aromatic), 1.0; F (in P–F), 1.50; F (in alkane), 1.47; Cl, 1.76; Br, 1.85; I, 1.96; O, 1.50; C (aliphatic), 1.70; C (aromatic), 1.77; N (single, double), 1.55; N (triple), 1.4–1.7; P, 1.80; S (single), 1.80; S (double), 1.75. van der Waals rotational boundary profiles estimated by this method are shown in Figure 3. The axial distance shown in Figure 3 refers to the distance along the primary rotational axis of the bond, measured from the covalent boundary of the supporting heteroatom.

Calculation of Steric Interactions in Polyphosphazenes.
—The various interactions between the groups attached

(22) Except where stated, average values were taken from the tabulated data of G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp 695–784, and P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

(23) Average values obtained from sources listed in ref 2 and 14.

to the phosphazene skeleton were estimated by scale geometrical and graphical methods using the average parameters listed above. The graphical model (Figure 4) and the side group boundary profiles (Figure 3) were then used to measure the area of lateral steric overlap between the different groups. (A volume overlap parameter, which might represent a more realistic measure of repulsion, would be far less readily calculated.) Overlap areas were estimated either by counting squares or, for large areas, by use of a planimeter. All interactions which fell within the boundary of the supporting phosphorus atom were neglected. The values shown in Table I are for overlap of two side groups in the a-type repulsion, for overlap of four groups (excluding diagonal interactions) in the c-type repulsion, and for overlap of two side groups with the 1:4 nitrogen atom in the d-type repulsion. Although, in this latter interaction, the van der Waals radius of nitrogen merges with those of the two adjacent phosphorus atoms, for the present purposes the nitrogen atom is considered as an isolated sphere.

Limitations of the Method.—The basic assumption of this approach is that intramolecular interactions can be predicted qualitatively on the basis of the repulsions which arise when spherical atomic van der Waals boundaries overlap. Such spherical symmetry is not found in practice, however, particularly along the axis of each bond. This would lead to discrepancies
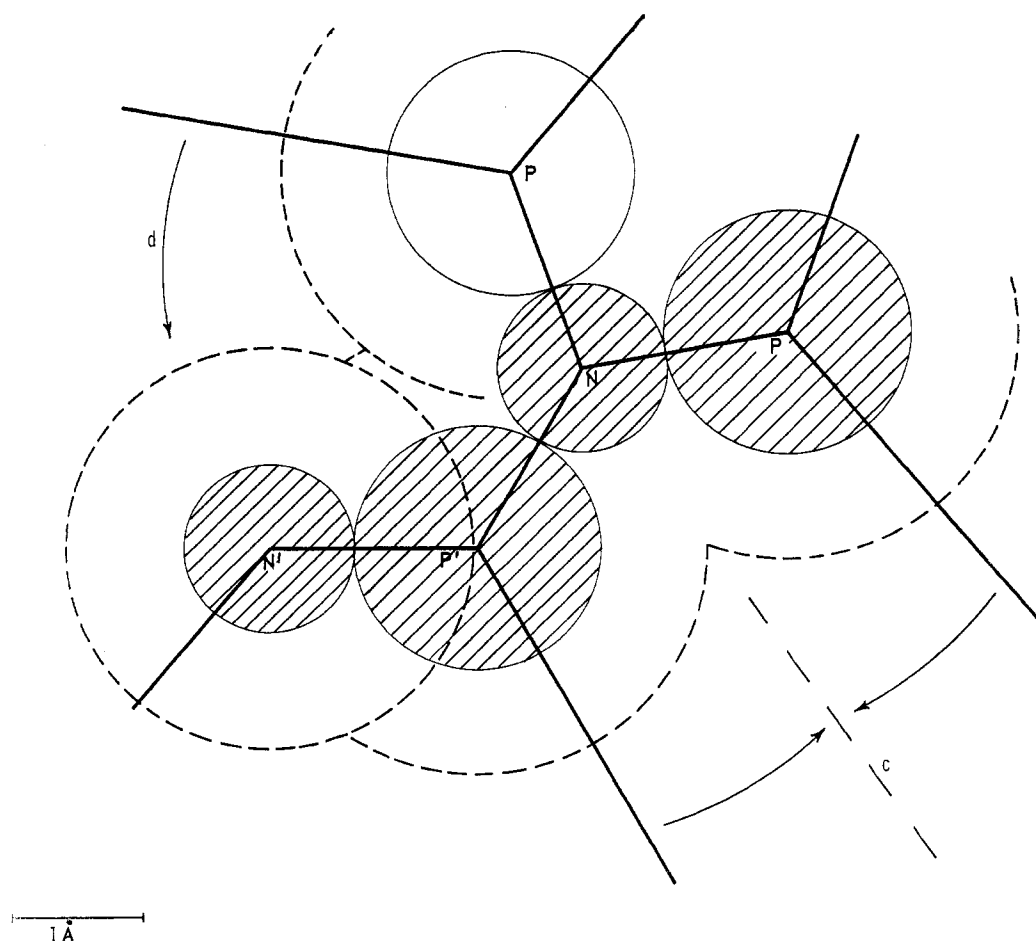
Figure 4.—Scale graphical model of phosphazene chain, showing van der Waals radii and side-group axes.

TABLE I

VAN DER WAALS STERIC OVERLAP PARAMETERS (A^2)
FOR PHOSPHAZENES[a]

Side group	a	c^b	d^{b-d}
H	...	...	...
F	...	...	...
Cl	0.04	0.2	...
Br	0.08	0.8	...
I	0.06	1.4	...
NH_2	0.04	1.5	...
SCN	0.06	14.8	...
CH_3	0.3	3.1	0.1
NCS	0.5	19.4	0.4
CF_3	1.5	9.3	1.5
C_6H_5	2.5	19.4	2.4
m-$(CH_3)C_6H_4$	2.6	43.0	2.5
$NH(CH_3)$, $N(CH_3)_2$	3.5	15.8	3.5
OCH_3	4.9	18.4	4.6
C_2H_5	5.3	21.0	5.0
o-$(CH_3)C_6H_4$	12.7	44.0	10.1
OC_2H_5	15.0	53.0	12.2
n-C_3H_7	15.2	53.4	12.0
$N(C_6H_5)$, $N(C_6H_5)_2$	21.5	81.6	12.3
OCH_2CF_3	21.9	72.8	13.9
OC_6H_5	24.2	85.6	13.5
n-C_4H_9	32.3	103.4	14.8

[a] Excluding all interactions within van der Waals boundary of supporting P atom. [b] Values give total overlap areas for *two* side groups per phosphorus atom. [c] For *cis–trans*-planar polymer configuration. [d] There is no d-type interaction between van der Waals radii of P and N in this system.

in the a-type overlaps predicted by the present method. Furthermore, the fact that electron-correlation effects are most important for a-type interactions introduces a further source of error for these particular predictions.

In addition, the present approach does not take into account the electrostatic dipolar repulsions which would be particularly significant for the c- and d-type interactions when halogeno, methoxy, or isothiocyano groups are present. The c and d values calculated here do, in fact, provide a rough measure of the repulsions which arise from the interpenetration of electron clouds and of the entropic repulsion which results from a reduction in the number of accessible conformations.

It is not possible to assign accurate energy equivalents to the calculated overlap areas. However, a rough measure of the energies involved for small c-type overlaps can be estimated from semiempirical potential functions recorded in the literature.[14d, 20] For example, the use of such relationships for the Cl··· Cl and H···H interactions suggests that the 0.2-A^2 c-type overlap in $(NPCl_2)_n$ corresponds roughly to about 2 kcal/repeating unit, and the 3.1-A^2 overlap in $[NP(CH_3)_2]_n$ corresponds to about 100 kcal/repeating unit. For larger overlap areas, for instance with the 9.3-A^2 c-type value obtained for $[NP(CF_3)_2]_n$, the F···F repulsion energy amounts to more than 50,000 kcal, and this indicates that the *trans-*

planar conformation is virtually impossible in this polymer. The fact that mixed potential functions ($H \cdots N$, $F \cdots N$, or $Cl \cdots N$, etc.) are involved in the d-type interaction renders the calculation of equivalent energies for the *cis–trans*-planar conformation much more difficult. Here again, a direct correlation of overlap area with repulsion energy leads to abnormally high energy values when the overlap exceeds perhaps 5 A^2. The fact that phosphazene polymers with bulky side groups can be synthesized at all indicates that the minimum repulsion energy per repeating unit must be less than about 500 kcal, and it is clear that the energy is minimized by bond stretching, bond angle distortion, and limitation of the torsional modes of the side groups to the most stable conformation.

Results and Discussion

Calculated Order of Steric Interactions.—The overlap parameters shown in Table I are placed in the order of increasing a- and d-type repulsions. This order should represent a decreasing oligomer polymerization tendency and an increasing depolymerization tendency, if steric effects are the predominant influence on equilibration. The data in Table I also demonstrate that, except for the yet unsynthesized poly(dihydrophosphazene) and for poly(difluorophosphazene), the d-type interaction invariably offers less opportunity for steric repulsion than does the c-type interaction. The *cis–trans*-planar form of the polymer may thus be expected to represent a more stable configuration than the *trans*-planar form. Models suggest that if c-type repulsions exist, the *gauche* orientation is of intermediate stability. It is possible that, when the overlap is small, the c and d differences may be ascribed to the approximations used for the measurements. However, recent evidence has been provided that poly(dichlorophosphazene), $(NPCl_2)_n$, exists in an approximately *cis–trans*-planar configuration,[14d] a result which is consistent with the steric calculations and with the expected skeletal polar attractions. When larger side groups are present, the difference between the c and d parameters is so great that it must represent a considerable steric inducement for the chain to adopt a *cis–trans*-planar conformation.[24]

Comparison with Experimental Data.—Quantitative polymerization or depolymerization data are almost nonexistent for phosphazene compounds, but a significant number of qualitative results have been described, and it is instructive to compare this information with the calculated parameters described above.

The steric overlap parameters divide the side groups into three general divisions—those in which the a and d interactions in the polymer are absent or negligible (overlap areas less than 1 A^2, including the groups H, F, Cl, Br, I, NH_2, CH_3, SCN, and NCS), those of intermediate repulsion (overlap areas below about 5 A^2, such as the groups CF_3, C_6H_5, OCH_3, m-$(CH_3)C_6H_4$, $NH(CH_3)$, $N(CH_3)_2$, and C_2H_5), and the highly hindered

systems with both a and d overlaps in the 10–30-A^2 range, such as the groups o-$(CH_3)C_6H_4$, OC_2H_5, n-C_3H_7, $NH(C_6H_5)$, $N(C_6H_5)_2$, OCH_2CF_3, OC_6H_5, and n-C_4H_9.

Polymerization.—The first category includes those compunds, such as $(NPF_2)_3$, $(NPF_2)_4$,[25] $(NPCl_2)_3$, $(NPCl_2)_4$,[26] $(NPBr_2)_3$, and $(NPBr_2)_4$,[27] which polymerize to high polymers when heated above 200–250°. The polymerization of $(NPCl_2)_{3-7}$ is exothermic with $-\Delta H$ decreasing with increasing ring size.[28] The compounds $[NP(NCS)_2]_3$ and $[NP(NCS)_2]_4$ also polymerize near 150°,[29] but the structure of the polymer has not been unambiguously established. The methylphosphazenes, $[NP(CH_3)_2]_{3 or 4}$, decomposed rather than polymerized at 300 to 400°.[30] Other cyclic phosphazenes, in the second category, do not yield high polymers at elevated temperatures. For example, octaphenylcyclotetraphosphazene, $[NP(C_6H_5)_2]_4$, when heated to 320–500°, gave a mixture of trimer, pentamer, hexamer, and higher homologs of unspecified molecular weight,[31,32] and the ethyl analogs, $[NP(C_2H_5)_2]_{3 or 4}$, underwent side-group decomposition rather than polymerization when heated.[33] No polymers have been produced by ring-cleavage polymerization of phosphazene oligomers fully substituted by the most hindered side groups, in the third category, although a number of authors have reported attempted polymerizations. For example, the compound $[NP(OCH_2-CF_3)_2]_3$ was converted to the tetramer rather than the polymer after 50-hr refluxing at 340°.[34] The ethoxy derivatives $[NP(OC_2H_5)_2]_{3 or 4}$ rearranged at 200° to N-ethyl compounds and apparently did not polymerize.[35] The trimeric and tetrameric phenoxy derivatives, $[NP(OC_6H_5)_2]_{3 or 4}$, do not polymerize or decompose after 26 hr at 300°.[35,36] Furthermore, attempts to polymerize catalytically $[NP(OC_6H_5)_2]_3$ and to polymerize thermally $[NP(OC_3H_7)_2]_3$, $[NP(OC_4H_9)_2]_3$, and $[NP(OC_6H_{11})_2]_3$ at temperatures between 150 and 350° were unsuccessful.[37] There is thus a rough correlation between large side group overlap parameters and resistance to polymerization.

A rather striking demonstration of the influence of the a-type effect on polymerizability is provided by the thermal behavior of tris(*o*-phenylenedioxy)cyclotriphosphazene (IV) and tris(2,2'-dioxydiphenyl)cyclo-

(24) The repeat distance for $[NP(OCH_2CF_3)_2]_n$ is 4.8 A, and for $[NP(OC_2H_5)_2]_n$ it is 4.9 A, compared with the reported value of 4.92 A for $(NPCl_2)_n$ (ref 14d).

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(34) R. Ratz, H. Schroeder, H. Ulrich, E. Kober, and C. Grundmann, *J. Am. Chem. Soc.*, **84**, 551 (1962).

(35) B. W. Fitzsimmons and R. A. Shaw, *Proc. Chem. Soc.*, 258 (1961).

(36) A measure of the unique stability of $[NP(OC_6H_5)_2]_3$ is provided by the fact that no fragmentation is observed when this material is volatilized at 250° into a mass spectrometer.

(37) M. Yokoyama, F. Yamada, S. Kawasaki, and K. Susuki, *Kogyo Kagaku Zasshi*, **66**, 613 (1963).

triphosphazene (V).[38,39] Compound IV polymerizes in the 250–350° temperature region, and the product has been shown to be an open-chain or macrocyclic polymer of molecular weight 13,000, formed by P–N ring cleavage. The 2,2'-dioxydiphenyl derivative (V) did not polymerize under similar conditions. The c and d overlaps in the polymer from IV are 0.16 A^2 and zero, while those in the polymer from V are 0.12 A^2 and zero, respectively (assuming that twisting of the diphenyl unit is minimal). These values are comparable to those in $(\text{NPCl}_2)_n$ and the differences between IV and V can, therefore, be ascribed to the change in the O–P–O bond angle. In IV, the presence of the five-membered cyclic structures at phosphorus decreases the external bond angle,[40] while in V the external angles would be widened even more than in $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$.

Depolymerization.—The available depolymerization data provide what is perhaps a more convincing demonstration of the steric influence on equilibration. Polydifluorophosphazene, $(\text{NPF}_2)_n$, and polydichlorophosphazene, $(\text{NPCl}_2)_n$, depolymerize to cyclic oligomers above 350°.[25,41–43] This temperature does not represent a ceiling temperature, however, since depolymerization is effected by continuous removal of volatile oligomers under nonequilibrium conditions.[44] The ceiling temperature of $(\text{NPCl}_2)_3$ may, in fact, be closer to 600° at pressures near 1 atm under equilibrium conditions.[41,43] It has also been reported that the methyl derivative, $[\text{NP}(\text{CH}_3)_2]_n$, depolymerizes to cyclic species in the 300–500° region.[45] The steric parameters shown in Table I suggest that the behavior of the fluoro-, chloro-, and methylphosphazenes represents the maximum thermodynamic depolymerization stability which might be expected for linear, high-polymeric phosphazene derivatives.[46] This is confirmed by the thermal behavior of other high molecular weight polyphosphazenes.[47] Experiments with $[\text{NP}(\text{OCH}_3)_2]_n$, $[\text{NP}(\text{OCH}_2\text{CH}_3)_2]_n$, $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$, $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$, and $[\text{NP}(\text{NHC}_6\text{H}_5)_2]_n$ indicate that these polymers undergo a rapid molecular weight decrease between 100 and 150°. Although the mechanism and products of these decomposition reactions have not been fully examined, the preliminary evidence indicates that the degradation products are predominantly low molecular weight homologs. These results indicate that, where R is OCH_3, OC_2H_5, OCH_2CF_3, NHC_6H_5, and OC_6H_5, the high polymers are thermodynamically unstable near 100°.

(38) H. R. Allcock, *J. Am. Chem. Soc.*, **86**, 2591 (1964).

(39) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1016 (1966).

(40) The O–P–O angle in IV is 97°: L. A. Siegel and J. H. van den Hende, private communication. The Cl–P–Cl angle in $(\text{NPCl}_2)_3$ is 103° (ref 14).

(41) O. Schmitz-Dumont, *Z. Elektrochem.*, **45**, 651 (1939).

(42) F. Patat and P. Derst, *Angew. Chem.*, **71**, 105 (1959).

(43) J. R. Soulen and M. S. Silverman, *J. Polymer Sci.*, **1**, 823 (1963).

(44) It must be emphasized that experiments based on the temperature at which oligomers can be distilled from a polymer provide very little information about the equilibrium thermal stability of the polymer. Such results and those obtained by thermogravimetric weight loss are more a measure of the volatility of the lower homologs formed by continuous equilibration of the system or of the boiling points of species formed by depolymerization at a lower temperature.

(45) H. H. Sisler, S. E. Frazier, R. G. Rice, and M. G. Sanchez, *Inorg. Chem.*, **5**, 326 (1966).

(46) The polymer, $[\text{NP}(\text{CF}_3)_2]_n$, is stable up to 380° (C. P. Haber, Chemical Society Special Publication No. 15, International Symposium on Inorganic Polymers, Nottingham, England, July 18–21, 1961, p 119), but whether this represents a depolymerization or a fragmentation temperature was not reported.

(47) H. R. Allcock and R. L. Kugel, unpublished results, and *J. Am. Chem. Soc.*, **87**, 4216 (1965). These high molecular weight, uncross-linked, soluble polymers were analytically pure, fully characterized materials, with molecular weights in the 1,000,000–3,000,000 range. The details of their synthesis and characterization will be reported subsequently. The depolymerization experiments were performed under vacuum, air, or nitrogen within sealed tubes and the molecular weight change was followed by the decrease in solution viscosity.