

Synthesis and Structure of Adamantane-Containing Phosphazenes

Wendy E. Krause, Masood Parvez,
Karyn B. Visscher, and Harry R. Allcock*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received June 14, 1996

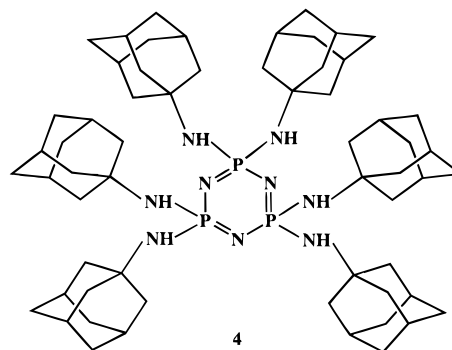
Adamantane (tricyclo[3.3.1.1^{3,7}]decane) is a highly symmetric, thermodynamically stable cage compound with the same structure as a diamond lattice. The unusual structure of adamantane imparts many useful chemical and physical properties, such as high thermal and oxidative stability, extreme lipophilicity, low surface energy, and high density.¹ Adamantyl groups have been incorporated into both the main and side chains of polymers in an effort to take advantage of the desirable properties resulting from the adamantane structure.² These polymers tend to demonstrate improved thermal resistance and oxidative stability, raised melting point and glass transition temperature, high dimensional stability, and improved solvent or hydrolysis stability. One of our long-range objectives is the synthesis of high molecular weight polyphosphazenes with adamantyl side groups, an objective that requires the prior exploration of synthesis approaches via small-molecule, model compound studies.

Hexachlorocyclotriphosphazene (**1**) and octachlorocyclotetraphosphazene (**2**) undergo a ring-opening polymerization when heated at 250 °C to form poly(dichlorophosphazene) (**3**).³ The chlorine atoms of species **1–3** can be replaced by organic side groups via nucleophilic substitution reactions.⁴ The reactions and structures of cyclic phosphazenes, such as **1** or **2**, are useful models to develop similar chemistry at the high polymeric level. We report here the first synthesis of adamantan-amino-containing phosphazenes. Work is currently in progress on other related adamantyl substituted phosphazenes, namely adamantanyloxy- and adamantylmethoxy-substituted species.

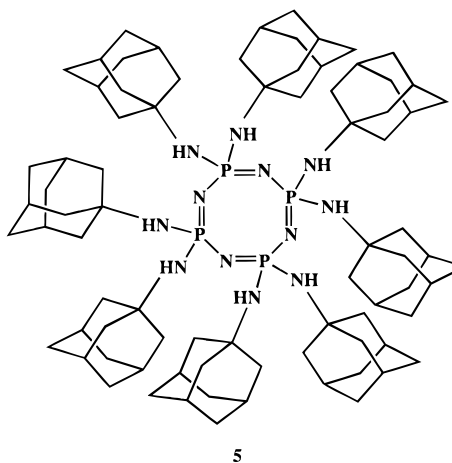
Hexakis(adamantan-amino)cyclotriphosphazene (**4**), octakis(adamantan-amino)cyclotetraphosphazene (**5**), and poly[bis(adamantan-amino-co-trifluoroethoxy)phosphazene] (**6**) have been synthesized. Compounds **4** and **5** were prepared by reaction of **1** or **2** with 2 mol of adamantanamine per chlorine in refluxing toluene. Triethylamine was present as a hydrochloride acceptor. The reaction of adamantanamine with the cyclic tetramer (**2**) yields a single, fully substituted product (**5**). In contrast, the reaction of adamantanamine with the cyclic trimer (**1**) results in a mixture of two products: the tetra-substituted product, *gem*-tetrakis(adamantan-amino)dichlorocyclotriphosphazene (**7**), and the fully substituted product **4**. Compound **4** was isolated in approximately 5% yield. Compounds **4** and **7** were separated by Soxhlet extraction with acetone. Compound **4** remained in

the thimble and **7** was concentrated into the solution phase. Compound **4** was then crystallized by the slow evaporation of deuterated chloroform from a concentrated solution.

Adamantyl groups are extremely bulky, and therefore it is not surprising that the reaction between **1** and adamantanamine gives only a small percentage of the fully substituted product (**4**). The fact that the tetramer reaction yields only the fully



substituted product (**5**) is more surprising. The cyclic tetrameric



phosphazene ring has a slightly higher degree of flexibility than the cyclic trimer. This increases the probability that the adamantanamine nucleophile can approach the remaining P–Cl units in a favorable manner, and thus, allow the reaction to proceed to the fully substituted product.

The molecular structure determined for **4** is shown in Figure 1 with selected bond lengths and angles listed in the caption.⁵ Two adamantan-amino groups are bonded to each phosphorus and one molecule of deuterated chloroform is included in the unit cell (not shown). The phosphazene ring in **4** is slightly puckered ($\chi^2 = 900$ for the weighted least-squares plane through the phosphazene ring). This puckering probably arises from steric interactions between the large adamantyl groups. Work toward solving the X-ray crystal structure of **5** is in progress.

By monitoring of the reaction of adamantanamine with **1** by ³¹P NMR spectroscopy,⁶ a geminal pattern for the addition of

- (1) (a) Fort, R. C.; Schleyer, P. R. *Chem. Rev.* **1964**, *64*, 277–300. (b) Tomimaga, K.; Haga, M. *Chem. Econ. Eng. Rev.* **1985**, *17*(10), 23–29.
- (2) For example: (a) Chern, Y.-T.; Chung, W.-H.; *J. Polym. Sci.: Part A* **1996**, *34*, 117–124. (b) Jensen, J. J.; Grimsley, M.; Mathias, L. J. *J. Polym. Sci.: Part A* **1996**, *34*, 397–402. (c) Malik, A. A.; Baum, A. K.; Unroe, M. R. *J. Polym. Sci.: Part A* **1992**, *30*, 1747–1754. (d) Matsumoto, A.; Tanaka, S.; Otsu, T. *Macromolecules* **1991**, *24*, 4017–4024. (e) Nozaki, K.; Kaimoto, Y.; Takahashi, M.; Takechi, S.; Abe, N. *Chem. Mater.* **1994**, *6*, 1492–1498.
- (3) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216–4218.
- (4) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709–1715.

- (5) Crystal data for **4** at 296 K: formula C₆₀H₉₆N₉P₃CDCl₃, triclinic, space group: *P*1̄ (No.2) with *a* = 12.720(3) Å, *b* = 13.10(2) Å, *c* = 19.04(2) Å, α = 77.3(1)°, β = 87.47(5)°, γ = 82.48(5)°, *V* = 3067(5) Å³, and *Z* = 2, 6230 data with *I* > 3 σ *I*, measured on an Enraf-Nonius diffractometer equipped with graphite-monochromated Mo K α radiation. The structure was solved by direct methods and refined by full-matrix least-squares calculations to *R* = 0.087, *R*_w = 0.088.

- (6) High-field ³¹P (146 MHz) NMR spectra were run on a Bruker WM360 spectrometer. ³¹P NMR spectra were proton decoupled and referenced to external 85% H₃PO₄ with positive shifts recorded downfield of reference.

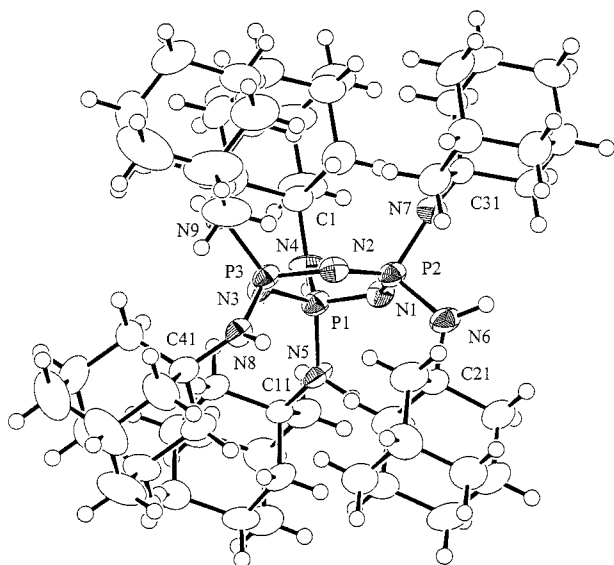
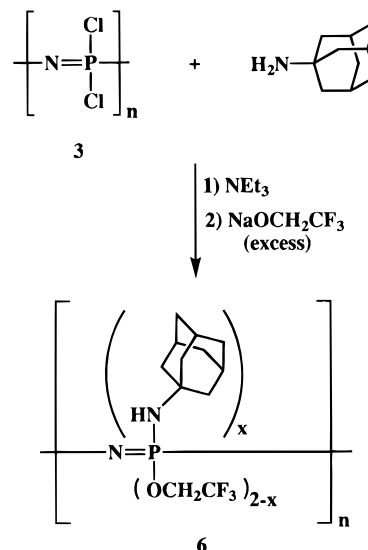


Figure 1. Crystal structure of **4**. Selected bond lengths (Å) and angles (deg): P(1)–N(1) = 1.576(6), N(1)–P(2) = 1.613(5), P(2)–N(2) = 1.567(6), N(2)–P(3) = 1.602(6), P(3)–N(3) = 1.604(5), N(3)–P(1) = 1.568(6), P(1)–N(4) = 1.666(6), P(1)–N(5) = 1.657(5), P(2)–N(6) = 1.668(6), P(2)–N(7) = 1.622(6), P(3)–N(8) = 1.625(6), P(3)–N(9) = 1.652(5); P(1)–N(1)–P(2) = 124.9(4), P(2)–N(2)–P(3) = 122.6(3), P(3)–N(3)–P(1) = 123.4(4), N(1)–P(2)–N(2) = 115.8(3), N(2)–P(3)–N(3) = 116.7(3), N(3)–P(1)–N(1) = 115.2(3).

this bulky amine was detected. In the early stages of the reaction, a doublet at +18.2 ppm and a triplet at +1.1 ppm appear in the ^{31}P NMR spectrum. These peaks and splitting pattern correspond to *gem*-bis(adamantanamino)tetrachlorophosphazene (**8**). The disubstituted phosphorus gives rise to the triplet, while the doublet was assigned to the two unsubstituted phosphorus atoms. With time a doublet at +3.4 ppm and a triplet at +19.3 ppm began to grow in as the other doublet and triplet decreased in intensity. The doublet at +3.4 ppm was assigned to the two disubstituted phosphorus atoms of **7**, while the triplet at +19.3 ppm arises from the unsubstituted phosphorus.⁷

Aminolysis reactions with **1** have been shown to be kinetically controlled.⁸ Geminal and non-geminal reactions take place concurrently and competitively via separate reaction mechanisms. The mechanism for the nongeminal substitution is associative ($\text{S}_{\text{N}}2$), while the geminal reaction appears to involve a rate-determining ionization step prior to attack by the nucleophile ($\text{S}_{\text{N}}1$). It has been concluded that the ratio of rates of the two reaction pathways depends on the rate of the

Scheme 1



nongeminal reaction, which is a function of the size of the amine. In the case of adamantanamine, the amine is sufficiently bulky that the nongeminal (associative) pathway may be effectively blocked, and so the reaction appears to proceed in a strictly geminal ($\text{S}_{\text{N}}1$) manner.

Adamantanamine also reacts readily with poly(dichlorophosphazene) (**3**) to give a partially substituted polymer. The reaction of **3** with excess adamantanamine in THF with triethylamine results in roughly 50% replacement of the chlorine atoms, as estimated by ^{31}P NMR spectroscopy. In phosphazenes a large percentage of unsubstituted phosphorus–chlorine bonds leads to hydrolytic instability unless the remaining chlorine atoms are replaced by a second nucleophile. Fully substituted, stable, mixed-substituent polymers can be formed by the subsequent reaction of the partially substituted polymer with excess sodium trifluoroethoxide, as shown in Scheme 1.⁹ Polymers with 1:4 and 1:1 ratios of adamantanamine to trifluoroethoxy side groups have been synthesized. These polymers are film-forming materials. The full characterization and examination of the physical properties of these polymers, especially as membranes, is underway.

Acknowledgment. We thank the U.S. Army Research Office for support of this work.

Supporting Information Available: Text giving experimental details of the structure determination and tables of crystallographic data, positional and displacement parameters, bond distances and angles and least squares planes are available (39 pages). See any current masthead page for ordering information and Internet access instructions.

IC960721S

(9) Structure shown for **6** is not meant to depict the actual phosphorus–substituent substitution pattern. There are also Ad–P–Ad and TFE–P–TFE linkages in the polymer.

(7) The ^{31}P NMR shift of **4** is +7.2 ppm and **5** is –4.39 ppm. Both were run in CDCl_3 .

(8) (a) Mack, D. P. Ph.D. Thesis, The Pennsylvania State University, Sept 1972. (b) Goldschmidt, J. M. E.; Licht, E. *J. Chem. Soc., A* **1971**, 2429–2434. (c) Goldschmidt, J. M. E.; Licht, E. *J. Chem. Soc., Dalton Trans.* **1972**, 728–732. (d) Goldschmidt, J. M. E.; Licht, E. *J. Chem. Soc., Dalton Trans.* **1972**, 732–736.