of square-planar complexes in solution involves the generation of a five-coordinate adduct which is proposed to be a labile configuration.[13] Isomerization can be effected photochemically in solution *via* an excited state postulated to be a triplet state of tetrahedral geometry. However, in solution both thermal and photochemical substitution reactions studied to date precede with retention of initial geometry.[14] It is possible that the production of *trans*-$Pt(MIM)_2Cl_2$ from *cis*-$[Pt(NH_3)_2(MIM)_2]Cl_2$ is a two-stage process in which isomerization and substitution are not concurrent. When structural studies of the product molecule now underway are complete, it may be possible to clarify this aspect of the solid-state chemistry of these square-planar complexes.

Acknowledgments.—The authors wish to acknowledge a valuable discussion with Professor R. W. Perry, Minot State College. We are also grateful to the University of Arkansas for providing computer facilities for this work.

[13] P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 4996 (1970).

[14] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y , 1967, p 377; V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970, p 247 ff.

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Phosphonitrilic Compounds. XIII.[1] The Structure and Properties of Poly(difluorophosphazene)[2]

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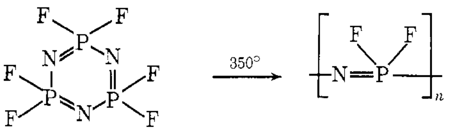
X-Ray diffraction investigation of oriented fibers of high molecular weight poly(difluorophosphazene), $(NPF_2)_n$, revealed the presence of two molecular conformers. Conformer A, with a chain repeating distance of 6.49 Å, was detected at temperatures between +25 and −36°. Conformer B, observed near −56°, showed a fiber (*c*) axis repeat of 4.86 Å. An orthorhombic unit cell (space group $Cmc2_1$) was assigned with a = 8.69 Å and b = 5.38 Å. Structure factor calculations for conformer B indicated a cis,trans-planar chain conformation, with P–N = 1.52 Å, P–F = 1.47 Å, F–P–F = 95°, N–P–N ≈ 119°, and P–N–P ≈ 136°. The low-temperature flexibility and high-temperature depolymerization of this polymer were also studied.

Results and Discussion

Poly(difluorophosphazene) (II) was first reported by Seel and Langer[3] as a product formed by the high-temperature polymerization of hexafluorocyclotriphosphazene (I). In view of the developing interest in phosphazene high polymers, this compound is of structural importance, since it contains a minimum number of atoms per monomer unit and provides a basis for the analysis of the more complex organo-substituted derivatives.



I II

We have undertaken an X-ray crystallographic examination of this compound with a view to determining the structure and chain conformation. Additional descriptive data have been obtained by ^{19}F nmr, differential thermal analysis, and depolymerization experiments.

Description of the Polymer.—Poly(difluorophosphazene) was prepared by the high-pressure, thermal polymerization of hexafluorocyclotriphosphazene (see Experimental Section). The polymer was a pale amber, rubbery elastomer. When exposed to atmospheric moisture it degraded rapidly with a loss of elasticity and formation of phosphoric and hydrofluoric acids. The polymer was insoluble in common organic solvents, but it swelled in hexadecafluoro-*n*-heptane in a manner characteristic of a lightly cross-linked polymer. The elemental analysis and infrared spectra were consistent with structure II (see Experimental Section).

The ^{19}F nmr spectrum of the swelled polymer consisted of a doublet at +70.5 ppm (relative to $CFCl_3$) due to spin–spin coupling with ^{31}P. No fine structure from coupling with nearby PF_2 units was observed. The chemical shift value was in good agreement with the values of +71.9 and +72.3 ppm reported for $(NPF_2)_3$ and $(NPF_2)_4$, respectively.[4]

The measured coupling constant J_{PF} of 878 cps for II was comparable to the values of 868 cps reported for $(NPF_2)_3$ and $(NPF_2)_4$.[4] The sharp doublet spectrum of solid II persisted at temperatures between +20 and −60°, and it must be assumed that conformational averaging of the fluorine environments takes place even at −60°. Thus, the barriers to internal rotation are small.

Restriction of backbone torsional motion normally occurs below the glass transition temperature (T_g) of a polymer. Thermomechanical measurements indicated that poly(difluorophosphazene) changes from a rubber

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[1] Part XII: H. R. Allcock and E. J. Walsh, *J. Amer. Chem. Soc.*, **94**, 119 (1972).

[2] A preliminary report of this work has appeared: H. R. Allcock, G. Konopski, R. L. Kugel, and E. G. Stroh, *J. Chem. Soc. D*, 985 (1970).

[3] F. Seel and J. Langer, *Z. Anorg. Allg. Chem.*, **296**, 317 (1958).

[4] T. Chivers, R. T. Oakley, and N. L. Paddock, *J. Chem. Soc. A*, 2324 (1970).

to a glass between −83 and −95°. Differential thermal analysis curves[5] indicated a glass transition temperature at −96° and a crystalline melting temperature of −68°. This low T_g value is also indicative of low intramolecular repulsions in this polymer.[6]

Poly(difluorophosphazene) depolymerizes at elevated temperatures to yield low molecular weight cyclic homologs. Under vacuum at 300–400° the principal depolymerization product is the cyclic tetramer, $(NPF_2)_4$, together with smaller amounts of higher homologs believed to include the pentamer through octamer. However, the cyclic trimer $(NPF_2)_3$ was not detected among the depolymerization products. Thermogravimetric analysis curves for samples heated at 10°/min in nitrogen indicated an initial weight loss at 190° and a 100% weight loss at 420°, the smooth shape of the weight loss curve being consistent with a depolymerization process.

X-Ray Examination of II.—Crystallization of the polymer was detected by optical birefringence when thin fibers were stretched. Low-temperature X-ray diffraction photographs showed the existence of two different crystalline modifications. The first (conformer A) was obtained by a 300% elongation of the polymer followed by cooling to temperatures between +25° and −36°. Conformer B was obtained at the same elongation at temperatures near −56°. Within the higher temperature range, conformer A exists with the total exclusion of conformer B. At −56° the two most intense reflections of conformer A appear as very weak reflections along with the strong pattern characteristic of conformer B. Thus, there is an almost total interconversion of the two polymorphs between −36 and −56°.

X-Ray Analysis of Conformer A.—Photographs obtained from conformer A showed thirteen reflections (five *hk*0, five *hkl*, and three *hk*2). (See Table I.) The unit cell symmetry was judged to be orthorhombic or lower, but at least two orthorhomic cells were consistent with the limited data (a = 21.43 Å, b = 5.83 Å, c = 6.49 Å; or a = 11.75 Å, b = 11.25 Å, c = 6.49 Å). Both unit cells would contain twelve monomer units. The experimental data for this polymorph were inadequate for a structural analysis. However, the fiber axis repeating distance of 6.49 ± 0.05 Å indicates that at least three monomer units are contained in each repeating segment and that a helical rather than planar conformation must exist.

TABLE I

d SPACINGS FOR CONFORMER A (Å)

	Reflection	d_{obsd}	Intens		Reflection	d_{obsd}	Intens
*hk*0	1	5.621	m	*hkl*	3	2.03	m
	2	3.933	mw		4	1.69	m
	3	3.571	s		5	1.55	vw
	4	2.200	vvw	*hk*2	1	2.11	s
	5	1.800	vvw		2	1.83	m
hkl	1	3.30	s		3	1.57	m
	2	2.26	s				

Space Group and Structure of Conformer B.—Eighteen reflections were observed for conformer B (eleven *hk*0, four *hkl*, and three *hk*2), with the upper-level reflections being diffuse. The fiber axis repeating distance was 4.86 ± 0.05 Å, which corresponds closely to the value of 4.92 Å reported for poly(dichlorophosphazene), $(NPCl_2)_n$.[7] All the reflections could be indexed by reciprocal lattice methods for an orthorhombic cell of dimensions a = 8.69 Å, b = 5.38 Å, and c = 4.86 Å, with the following systematic presences: *hkl*, $h + k = 2n$; *hk*0, $h + k = 2n$; 0*k*0, $k = 2n$; *h*00, $h = 2n$; 00*l*, $l = 2n$ (Table II).

TABLE II

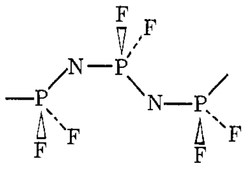
OBSERVED AND CALCULATED *d* SPACINGS FOR CONFORMER B (Å)

	d			*d*	
hkl	Calcd	Obsd	*hkl*	Calcd	Obsd
110	4.574	4.572	130	. . .	Unobsd
200	4.344	4.343	111	3.33	3.35
020	2.688	2.682	311	2.26	2.30[a]
310	2.550	2.552	021	2.34	
420	1.689	1.688	221	2.07	2.06
510	1.653	1.652	421	1.60	1.58
330	1.524	1.523	511	1.57	
600	1.448	1.447	131	. . .	Unobsd
040	1.344	1.342	002	2.58	2.61[b]
240	1.287	1.286	112	2.15	2.14
530	1.248	1.248	202	2.12	
220	. . .	Unobsd	312	1.78	1.77
400	. . .	Unobsd			

[a] Very diffuse reflection, possibly a doublet. [b] Very intense and very diffuse reflection.

The measured density at 25° of 1.84 g/ml, obtained by flotation techniques, was definitely too low to correspond to the crystalline regions of the polymer. If four monomer units are assumed to occupy the unit cell, the calculated density of 2.25–2.42 g/ml corresponds closely to the known densities of $(NPF_2)_3$ and $(NPF_2)_4$ (2.24 and 2.20 g/ml, respectively).[8,9] Unusually low observed densities have also been reported for $(NPCl_2)_n$.[7]

The systematic presences on the *hk*0 layer and for 00*l*, $l = 2n$, eliminate all but thirteen of the possible orthorhombic space groups, eight of which are *c* centered and five of which are primitive. The *c*-axis repeating distance of 4.86 Å strongly suggests that the polymer assumes a conformation close to cis,trans planar (III), with two monomer units per axial repeat. Thus, two chain molecules pass through each cell. This, coupled with the fact that two very intense *hk*0 reflections are observed at 200 and 110, indicates that the chains occupy the center and corners of the cell when viewed down the fiber axis.



III

Selected bond lengths and bond angles based on crystal structure studies of the cyclic trimer and tetramer, $(NPF_2)_{3\text{ and }4}$[8,9] (N–P = 1.51 Å, P–F = 1.52 Å, N–P–N = 120°, P–N–P = 137°, F–P–F = 99.9°),

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[5] We are indebted to Dr. E. Schmidt of American Cyanamid Co., for the dta and tga curves.

[6] H. R. Allcock, J. E. Lehnsen, and J. J. Meister, unpublished calculations.

[7] K. H. Meyer, W. Lotmar, and G. W. Pankow, *Helv. Chim. Acta*, **19**, 930 (1936).

[8] M. W. Dougill, *J. Chem. Soc.*, 3211 (1963).

[9] H. McD. McGeachin and F. R. Tromans, *ibid.*, 4777 (1961).

were used as a basis for a trial structure, with a cis,trans-planar chain conformation assumed. Consideration of models and optimum packing conditions showed that the molecule at the center of the cell must be related to the molecules at the corners by a 2_1 axis. This is consistent with space group *Cmc*2_1 (no. 36) as the most likely arrangement. Fourier calculations for the *hk*0 reflections, with the use of numerous trial model structures, indicated that the unit cell arrangement depicted in Figures 1 and 2 provided the best arrangement of atoms. The calculated and observed intensities based on this structure are in good agreement with each other (Table III).[10]

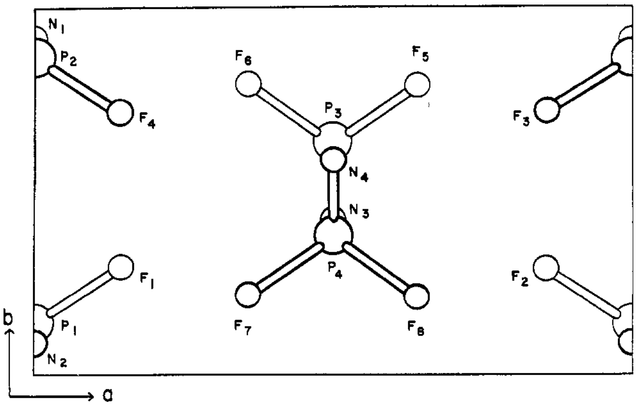

Figure 1.—Projection of atoms in the unit cell of poly(difluorophosphazene) (conformer B), viewed down the fiber (*c*) axis.

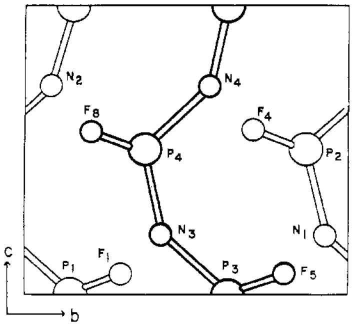

Figure 2.—Projection of the atoms in part of the unit cell of poly(difluorophosphazene) (conformer B), viewed down the *a* axis.

Final refinement of the atoms by trial and error methods led to the atomic positions indicated in Table IV, with the bond lengths and angles given in Table V. The chains occupy an exact cis,trans-planar conformation. Fourier calculations gave an *R* factor based on structure factors of 16.1, but if the three most intense reflections were neglected, the *R* value was 24.0. Use of the intensities yielded an *R* value of 13.5, and neglect of the three most intense reflections gave an *R* value of 21.3. In both cases, the higher *R* values are believed to be more appropriate since the three most intense reflections contribute more than half of the total intensity. However, these *R* values are considered to be satisfactory for a polymer structure.

TABLE IV

ATOMIC COORDINATES FOR CONFORMER B

		x	*y*	*z*
P	1	0	0.129	0
	2	0	0.871	0.5
	3	0.5	0.629	0
	4	0.5	0.371	0.5
N	1	0	0.915	0.203
	2	0	0.085	0.703
	3	0.5	0.415	0.203
	4	0.5	0.585	0.703
F	1	0.125	0.299	0.068
	2	0.875	0.299	0.068
	3	0.875	0.701	0.568
	4	0.125	0.701	0.568
	5	0.625	0.799	0.068
	6	0.375	0.799	0.068
	7	0.375	0.201	0.568
	8	0.625	0.201	0.568

TABLE V

BOND DISTANCES AND ANGLES (CONFORMER B)[a]

PN = 1.52 Å

PF = 1.47 Å

FPF = 95°

NPN = 119°

PNP = 136°

[a] Normal standard deviation calculations are not applicable to a structure determination of this type, but maximum values are estimated to be in the region: PN and PF, ±0.03 Å; FPF, ±2°; NPN and PNP, ±4°.

The final atomic parameters (Table IV) are likely to be more accurate in the *x* and *y* coordinates, than in the *z* parameter, since the *hk*0 Fourier calculations are independent of the *z* coordinate. The *z* coordinates assume importance only in the *hk*1 and *hk*2 reflections, and these are less numerous and more diffuse than their *hk*0 counterparts. This relative uncertainty in the *z* coordinate will have the greatest effect on the N-P-N and P-N-P bond angles. Thus, it should be recognized that the final skeletal bond lengths and angles do not have the reliability normally expected for a conventional single-crystal study.

It should also be noted that, although polymer structures can sometimes be solved by a consideration of helical diffraction theory,[11] such methods proved to be less satisfactory than standard Fourier techniques for this structure. This limitation was imposed, first, because few layer lines were detected and, second, because low-order Bessel functions were found on all layer lines. This latter factor reduced the sensitivity of the helical trial and error procedure to well below that of the conventional structure factor method.

Comparisons with Related Systems.—The only related polymer for which comparable data are available is poly(dichlorophosphazene), $(NPCl_2)_n$. This polymer yields sharp fiber diffraction patterns with at least 23 reflections,[7] but unambiguous assignment of the space group has not been made. However, optical transform techniques were used to postulate a helically distorted cis,trans-planar chain conformation.[12] A recent infrared study has provided some confirmation for this interpretation.[13]

The molecular structure of poly(difluorophosphazene)

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[10] Table III, showing observed and calculated structure factors and intensities for conformer B, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1120. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[11] (a) W. Cochran, F. H. C. Crick, and V. Vand, *Acta Crystallogr.*, **5**, 581 (1952); (b) D. R. Davies and A. Rich, *ibid.*, **12**, 97 (1959).

[12] E. Giglio, F. Pompa, and A. Ripamonti, *J. Polym. Sci.*, **59**, 293 (1962).

[13] T. R. Manley and D. A. Williams, *Polymer*, **10**, 307 (1969).

can be compared with those of the cyclic trimer and tetramer, $(NPF_2)_3$ and $(NPF_2)_4$. The bond lengths and the N–P–N and F–P–F bond angles are comparable in all three molecules, but marked differences exist in the P–N–P skeletal angles. In $(NPF_2)_3$ the P–N–P angles are 119.6 and 121.1°,[8] whereas in the tetramer the angle is 147.2°,[9] and in the high polymer it is ~136°. There is much evidence that in cyclophosphazenes the skeletal angle at nitrogen varies with the molecular restrictions imposed by the phosphazene ring. Both $(NPF_2)_3$ and $(NPF_2)_4$ have planar rings, and the P–N–P angles found result from the geometric requirements of the six- and eight-membered planar rings. However, the high polymer is not subject to these restrictions and the angle of ~136° presumably reflects more closely the hybridization requirements at nitrogen.

The ring planarity of $(NPF_2)_3$ and $(NPF_2)_4$ could reflect the influence of π' skeletal bonding in these molecules,[14,15] and the cis,trans-planar structure assumed by the polymer, at first sight, reinforces this view. However, it should be noted that the planar polymer conformation exists only at low temperatures and that, on the basis of the repeating distance, conformer A is definitely not planar. Thus, crystal-packing forces may be responsible for the observed conformations. van der Waals intermolecular contact distances calculated for conformer B are given in Table VI. The distances of the nearest F···F contact (3.28 Å) and F···N contact (3.39 Å) are comparable to those for the cyclic trimer and tetramer[8,9] (F···F trimer, 2.95 Å; F···F tetramer, 3.01 Å; F···N trimer, 3.30 Å; F···N tetramer, 3.49 Å). The fact that the F···N contacts are longer than predicted on the basis of van der Waals radii (3.05 Å)[16] may be a consequence of the orientation of the lone-pair orbital at nitrogen and perhaps also of a high charge density at fluorine.

TABLE VI

INTERMOLECULAR CONTACT DISTANCES (CONFORMER B)

F_1–F_6 = 3.46 Å

F_1–F_4 = 3.28 Å

F_1–F_7 = 3.33 Å

F_1–N_1 = 3.55 Å

F_6–N_1 = 3.39 Å

Experimental Section

Synthesis of Poly(difluorophosphazene) (II).—Hexafluorocyclotriphosphazene (I) was prepared by the interaction of hexachlorocyclotriphosphazene with sodium fluoride in acetonitrile solvent.[17] A purified sample of I (9.9 g, 0.0398 mol) was placed in a thick-walled Pyrex glass polymerization tube of 17-ml capacity, which was then attached to a vacuum line. The tube was cooled to −78°, evacuated to <1 mm pressure for 5 min, then isolated from the vacuum line by closure of the stopcock, and warmed to the melting point of I. This freeze–thaw procedure was carried out three times, and the tube was then sealed under vacuum. The tube was protected by a gauze safety screen and this assembly was placed in a 3-l. capacity, electrically heated autoclave. The autoclave was pressurized with nitrogen to 1920 psi, and the temperature was raised over a period of 90 min to 350°. The temperature was held at 350–360° for 14 hr, and the apparatus was then allowed to cool to 37° during 10 hr. The nitrogen pressure was released slowly and the polymerization tube was removed carefully with the usual safety precautions. The transparent, amber polymer was then stored under vacuum until used. *Anal.* Calcd for F_2NP: F, 45.79; N, 16.88; P, 37.33. Found: F, 45.50; N, 17.07; P, 35.49.

It should be noted that the vapor pressure of hexafluorocyclotriphosphazene at 350° is so high (~300 atm[18]) that conventional sealed-tube techniques cannot be employed without the creation of a serious pressure explosion hazard. Polymerization does not occur at an appreciable rate below 320°.

Properties of Poly(difluorophosphazene).—The density value of 1.84 g/ml was determined by flotation of a 1-mm unstretched cube in *n*-heptane–methyl iodide mixtures at 25°. Infrared spectra of thin films of the polymer were poorly resolved but with principal bands evident at 3150–3020 (doublet, m), 2760 (m), 1950–1920 (m), 1540–1250 (s), 1135 (m), 1110 (m), and 1010–630 cm^{-1} (b, s). The thermal depolymerization products from II were identified by vapor-phase chromatography, infrared spectra, and melting points.

^{19}F Nmr Spectra.—The chemical shift was measured with the use of a Varian HR 100 instrument with hexadecafluoro-*n*-heptane as a swelling agent and as an internal standard. The center of the fluorine doublet appeared at −14.0 ppm relative to the CF_3 absorption in the standard, and this was then converted to a shift value relative to trichlorofluoromethane. The variable-temperature work was conducted with the solid elastomer.

X-Ray Technique.—Thin fibers of the polymer (~0.5-mm diameter) were cut and mounted on a small brass stretching apparatus,[19] which held the fiber at a fixed extension ratio during X-ray studies. Crystallization was induced in the sample by annealing under tension at +150 to −78° in an atmosphere of dry nitrogen. Photographs were taken using Nonius cylindrical (general-purpose) cameras of diameter 114.6 and 57.3 mm. Low temperatures were obtained by introduction into the camera of a stream of cold dry nitrogen from a 50-l. reservoir of liquid nitrogen. Temperature regulation within ±2° was obtained by variations in the nitrogen boiling rate. Moisture was rigorously excluded from the camera by a polyethylene canopy to prevent hydrolysis of the sample. Standard stationary fiber-type photographs were obtained with nickel-filtered Cu Kα radiation (42 kV, 20 mA), using exposure times of 2, 4, 6, 8, 10, 20, 24, and 36 hr. Tilted fiber photographs and oscillation photographs with the axis of oscillation perpendicular to the fiber axis were also taken. Intensities were estimated by visual comparison with a standard scale, with each reflection corrected visually for differences in area. The scattering factors used were those compiled by Ibers.[20] Standard Lorentz, polarization, and multiplicity corrections were applied, and a B value determined by Wilson's method was 1.7 for conformer B.

Acknowledgment.—We thank the U. S. Army Research Office, Durham, N. C., for the support of this work.

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

[15] K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

[16] A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

[17] R. Schmutzler, *Inorg. Syn.*, **9**, 76 (1967).

[18] This estimate is based on the vapor pressure equation suggested by Schmutzler.[17] However, by assuming total vaporization at 0° and treating the resultant vapor as an ideal gas, the pressure is calculated to be ~150 atm.

[19] The design of this device was based on a model used by Dr. H. D. Noether of Celanese Research Laboratories.

[20] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 201–207.