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SYNTHESIS OF ETHYLENEDINITRAMINE DERIVATIVES OF FLUOROCYCLOTRIPHOSPHAZENES

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SYNTHESIS OF ETHYLENEDINITRAMINE DERIVATIVES OF FLUOROCYCLOTRIPHOSHAZENES

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Novel mono- and bis-spiro(ethylenedinitramino) derivatives of hexafluorocyclotriphosphazene have been synthesized and characterized by ^1H , ^{13}C , ^{31}P and ^{19}F NMR spectroscopy. The structure of 3,3,5,5-bis-spiro(N,N'-dinitroethylenediamino)-1,1-difluorocyclotriphosphazene has also been established by single crystal x-ray analysis.

Key words: Hexafluorocyclotriphosphazene, bis-spiro(ethylenediamino)cyclotriphosphazene, spiro(ethylenedinitramino)cyclotriphosphazene, bis-spiro(ethylenedinitramino)cyclotriphosphazene.

INTRODUCTION

Although there is abundant literature on the chemistry and reactions of hexachlorocyclotriphosphazene with mono and difunctional amines, the hexafluorocyclotriphosphazene system has received considerably less attention. In part, this may be due to the similar chemistry expected for hexachlorocyclotriphosphazene and its fluorine analog. However, there are instances, attributable to the strong P—F bond, when marked differences in the behavior of hexachlorocyclotriphosphazene and hexafluorocyclotriphosphazene are found. For example, polymerization of hexafluorocyclotriphosphazene requires appreciably higher temperature than its chlorine analog. Also, while phenylmagnesium bromide reacts with hex-

achlorocyclotriphosphazene to yield linear products and small amounts of the hexaphenyl derivative,^{1,2} the same reaction with hexafluorocyclotriphosphazene and the Grignard reagent affords products that are mostly mono- and geminal-diphenylcyclotriphosphazenes.³

The reaction of hexafluorocyclotriphosphazene with monofunctional amines such as $\text{Me}_2\text{NSiMe}_3$ and Me_2NH is known to give monoamino derivatives.⁴ Hexafluorocyclotriphosphazene reacts with the secondary difunctional amine, $\text{N,N}'$ -dimethylethylenediamine, through geminal substitution to give spiro($\text{N,N}'$ -dimethylethylenediamino)tetrafluorocyclotriphosphazenes.⁵ No such reaction is reported for primary difunctional amines.

We report here some reactions of hexafluorocyclotriphosphazenes with a primary diamine (i.e., ethylenediamine) followed by nitration of the products to obtain 3,3,5,5-bis-spiro($\text{N,N}'$ -dinitroethylenediamino)-1,1-difluorocyclotriphosphazene, **5**. The crystal density of this compound was then measured and compared with its chlorine analog. The N-nitro compounds are of significant interest in energetic materials research.

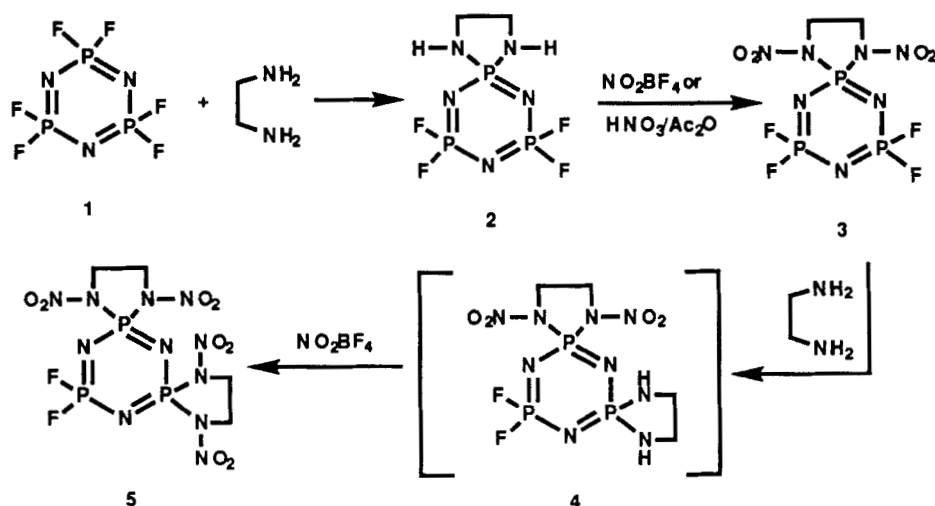
RESULTS AND DISCUSSION

The reactions of difunctional reagents with hexahalocyclotriphosphazenes are known to yield three different products: a) *bino* derivatives, resulting from the displacement of two halogens from phosphorus atoms in different rings leading to cyclo-linear polymers, b) *ansa* compounds, resulting from the displacement of two halogen atoms from different phosphorus atoms in the same ring and c) *spiro* derivatives, formed by the displacement of geminal halogen atoms on the same phosphorus atom. A large number of substituted cyclophosphazenes with *bino* and/or *ansa* and/or *spiro* configurations have been reported.⁶

As part of a continuing investigation in these laboratories of N-nitramines of various spiro-substituted ethylenediamine derivatives of cyclotriphosphazenes, two units of $\text{N,N}'$ -dinitroethylenediamine were introduced into hexafluorocyclotriphosphazene system, **1**, in a stepwise fashion (Scheme I).

Hexafluorocyclotriphosphazene **1** was treated with ethylenediamine in dichloromethane to give 1,1-spiro(ethylenediamino)-3,3,5,5-tetrafluorocyclotriphosphazene, **2**, in 71% yield. Compound **2**, was nitrated, using either nitronium tetrafluoroborate or acetic anhydride/100% nitric acid, to give 1,1-spiro($\text{N,N}'$ -dinitroethylenediamino)-3,3,5,5-tetrafluorocyclotriphosphazene, **3**. The second $\text{N,N}'$ -dinitroethylenediamine unit in **3** was introduced with spiro fusion, also in two successive steps. First compound **3** was treated with ethylenediamine to form the intermediate 1,1-spiro(ethylenediamino)-3,3-spiro($\text{N,N}'$ -dinitroethylenediamino)-5,5-difluorocyclotriphosphazene, **4**. This intermediate was then nitrated with nitronium tetrafluoroborate to give 1,1,3,3-bis-spiro($\text{N,N}'$ -dinitroethylenediamino)-5,5-difluorocyclotriphosphazene, **5**.

Preparation of **5** via trans-halogenation of its chlorine analog⁷ was unsuccessful and resulted in the ring opening of the $\text{N,N}'$ -dinitroethylenediamino adduct. Synthesis of tris-spiro($\text{N,N}'$ -dinitroethylenediamino)cyclotriphosphazene has already been reported.⁷



SCHEME 1

The compounds reported in this study were characterized by ^1H , ^{13}C , ^{31}P and ^{19}F spectroscopy. For example, the structure of 3,3,5,5-bis-spiro(N,N' -dinitroethylenediamino)-1,1-difluorocyclotriphosphazene, **5**, is reinforced by the observation of a signal at δ 43.1 in the ^{13}C spectrum. The complex multiplet ^1H resonances at δ 4.2 and δ 4.4 may be attributed to spin-coupling interactions between the two sets of magnetically non-equivalent protons in each of the nitramino rings which are further split by the strong (~ 46 Hz) three-bond $^1\text{H}-\text{C}-\text{N}-^{31}\text{P}$ coupling. The ^{19}F spectrum measured against C_6F_6 and reported relative to CFCl_3 shows triplets centered at -59.3 and -62.5 ppm due to the one-bond $^{31}\text{P}-^{19}\text{F}$ coupling of 912 Hz. The ^{31}P spectrum measured at 81 MHz is clearly non-first order and exhibits multiplets centered at 27.3, 16.2 and 6.0 ppm relative to external 85% H_3PO_4 . The ^{31}P spectrum could be fairly well-simulated using the following parameters: $^1J(^{31}\text{P}_1-^{19}\text{F}) = 912$ Hz, $^2J(^{31}\text{P}_1-^{31}\text{P}_2) = 2$ Hz, δ 5.8 ($^{31}\text{P}_1$) and δ 6.0 ($^{31}\text{P}_{2,3}$).

The structure of compound **5** was further unequivocally determined by X-ray crystallography (Figure 1). There are four independent molecules of **5** and one water molecule in the asymmetric unit of the crystal. The water lies in a cavity bounded by nitro-group oxygen atoms from each of the four molecules of **5**; there are six $\text{O} \cdots \text{O}$ contacts ranging from 3.2 to 3.7 Å. The hydrogen atoms on the water were not visible in X-ray difference electron-density maps, perhaps because the water can, by tumbling, form two weak hydrogen bonds to various pairs of nitro-oxygen atoms about the cavity. Indeed, the assignment of this peak as water is somewhat tentative; however, the inclusion of some type of small solvent in the cavity is strongly supported by the refinement. Including the water oxygen lowers the crystallographic agreement factor (R_w) from 0.077 to 0.040, a very significant improvement.

The phosphazene rings vary slightly in the four molecules because of differing packing environments, but all can be classified as almost-planar shallow boats. Individual atoms deviate from the ring plane by less than 0.15 Å (mean dev., 0.07 Å). The ring PN distances adjacent to the gem difluoro-phosphorus atom range

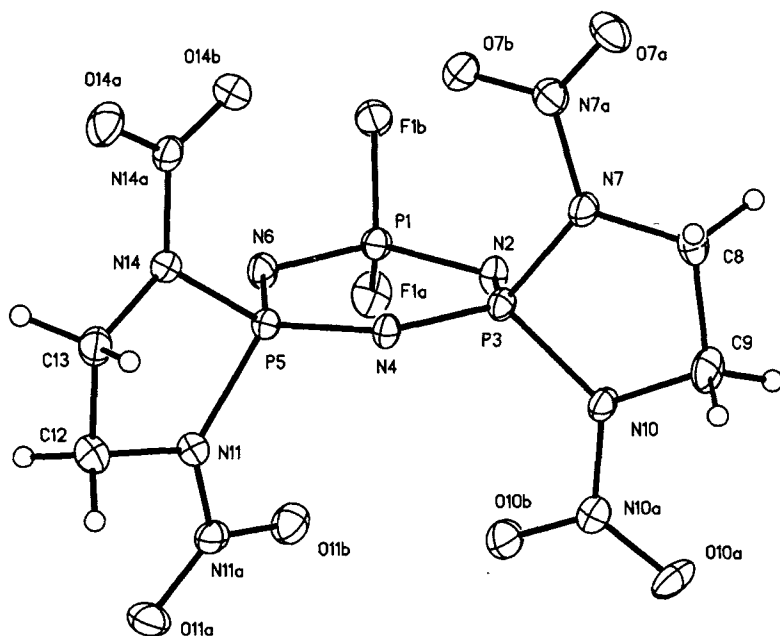


FIGURE 1 The molecular structure and numbering scheme for one of the four molecules of 3,3,5,5-Bis-spiro(N,N'-dinitroethylenediamino)-1,1-difluorocyclotriphosphazene found in the crystallographic asymmetric unit. The others were similar in conformations.

from 1.561 to 1.568 Å, and average 1.563 Å. Other ring PN distances range from 1.568 to 1.590, with an average 1.576 Å. Both of these averages fall well within the rather large range (1.55–1.67 Å) observed for ring bonds in 47 well-determined (X-ray $R < 0.07$) amino-substituted cyclotriphosphazenes found in the Cambridge Structural Database.⁸

The PF bond distances in the four molecules of **5** range from 1.514 to 1.527 Å (average: 1.523 Å). This is slightly (but not significantly) shorter than had been reported⁸ previously for three other bis(difluoro)cyclotriphosphazenes, where the PF distances range from 1.518 to 1.539 Å and average 1.527 Å. The F—P—F bond angles in **5**, 97.3 to 98.5°, are slightly larger, but not significantly different from reported values (96.3 to 97.4°) in similar compounds.⁹

The measured crystal density of compound **5** (1.913 mg/mm⁻³) is greater than that observed for its chlorine analog (1.898 mg/mm⁻³).

EXPERIMENTAL

Caution! The nitramino compounds are potentially explosive and must be handled behind an appropriate protective barrier. In all nitrations with nitronium tetrafluoroborate, upon removal of acetonitrile, the residue must immediately be quenched with water to destroy excess NO₂BF₄.

The ¹H NMR spectra and ³¹P NMR spectra were recorded on a Bruker 300 MHz spectrometer. The ¹⁹F NMR spectra were recorded on a Varian XL 200 instrument. The chemical shifts are reported in ppm downfield from internal tetramethylsilane for ¹H NMR spectra, from external phosphoric acid for ³¹P NMR spectra, and from external C₆F₆ for ¹⁹F NMR spectra. High resolution mass spectra were measured on a JOEL HX110A mass spectrometer by FAB ionization mode using peak matching. Hexafluorocyclotriphosphazene was made by following a literature procedure.¹⁰ Hexachlorocyclotri-

phosphazene and NaF were obtained from Aldrich Chemical Company and nitronium tetrafluoroborate from Ozark-Mahoning, Inc. Compound **4** exhibited instability in solution due to the presence of both H—N and P—F linkages and was nitrated in the subsequent reaction without further purification.

1,1-spiro(ethylenediamino)-3,3,5,5-tetrafluorocyclotriphosphazene, 2

To a solution of hexafluorocyclotriphosphazene (31 g, 124 mmol) was added a solution of ethylenediamine (24 g, 400 mmol) in methylene chloride (25 mL) in 1 hour. The reaction was exothermic and was maintained at 25°C. After stirring at 25°C for another 24 hours, the mixture was extracted with water. The organic phase was dried (MgSO₄), filtered, and the filtrate was concentrated under reduced pressure to give **2** as a white solid (24 g, 71%) mp 125°C. ¹H NMR (CDCl₃) δ 2.7(d, N-H, *J* = 10.8 Hz), 3.45 (d, CH₂, *J* = 12.6 Hz); ¹³C NMR (CDCl₃) δ 42.4 (d, *J* = 11.3 Hz); ³¹P NMR (CDCl₃) δ (0.64, 12.1, 22.5) (t, m, *J*_{P—F} = 882 Hz), 31.7 (t, t); HRMS (EI) calc. 268.977223; found *m/e* 268.9768.

1,1-spiro(N,N'-dinitroethylenediamino)-3,3,5,5-tetrafluorocyclotriphosphazene, 3

Method A: To a cooled solution (0°C) of compound **2** (11.2 g, 41.6 mmol) in acetonitrile (200 mL) was added NO₂BF₄ (12.1 g, 91.1 mmol). The solution was stirred at 25°C for one hour and then concentrated by rotary evaporation and to the residue was added ice-cold water (200 mL). The precipitated product, **3**, was collected by filtration (6.0 g, 40% yield).

Method B: To ice-cooled acetic anhydride (86 mL) was added very carefully 100% nitric acid (23 mL) dropwise over two hours. The solution was then stirred for one hour at 24°C and again cooled to 0°C and compound **2** (9.0 g, 33 mmol) was added in one portion. The resulting mixture was stirred at 0°C for two hours and then poured over ice and the precipitated product, **3**, was collected by filtration (9.1 g, 76%) mp 117°C. ¹H NMR (CDCl₃) δ 4.17 (d, *J* = 6.7 Hz); ¹³C NMR (CDCl₃) δ 41.47 (d, *J* = 9.7 Hz); ³¹P NMR (CDCl₃) δ (1.4, 11.7, 23.0) (t, m, *J*_{P—F} = 940 Hz), 4.2 (m); ¹⁹F NMR (CDCl₃) δ -66.9 to -63.7 (d, m, *J*_{F—P} = 934 Hz); HRMS (EI) calc. 358.947380; found *m/e* 358.9475.

1,1-spiro(ethylenediamino)-3,3-spiro(N,N'-dinitroethylenediamino)-5,5-difluorocyclotriphosphazene, 4

To a solution of **3** (0.5 g, 1.4 mmol) in CH₂Cl₂ (90 mL) was added ethylenediamine (1.0 g, 16.6 mmol). The solution was stirred at 25°C for two hours and then filtered; the filtrate was concentrated by rotary evaporation to give **4** as an oil (0.5 g, 1.3 mmol). This compound exhibited instability in solution and was used without further purification. ¹H NMR (acetone-d₆) δ 2.72 (t), 3.48 (t); ³¹P NMR (acetone-d₆) δ (4.8, 15.6, 26.3) (t, t, *J*_{P—F} = 875 Hz, *J*_{P—P} = 1.08 Hz), 34.26 (d); ¹⁹F NMR (acetone-d₆) δ -61.35 to -58.25 (d, t, *J*_{F—P} = 875 Hz).

1,1,3,3-Bis-spiro(N,N'-dinitroethylenediamino)-5,5-difluorocyclotriphosphazene, 5

To a solution of **4** (0.19 g, 0.5 mmol) in CH₃CN (35 mL) was added NO₂BF₄ (0.6 g, 4.5 mmol). The mixture was stirred at 25°C for 45 minutes and then concentrated by rotary evaporation to give a thick yellow oil which was partitioned between water and CHCl₃. The organic layer was separated, dried over MgSO₄ and concentrated by rotary evaporation to an oil. Diethyl ether was added to the oil; a precipitate began to form in about two minutes. The precipitate, **5**, was collected by filtration and dried to a constant weight (30 mg, 0.06 mmol, 12% yield) mp 209–211°C. ¹H NMR (acetone, d₆) δ 4.24 to 4.46 (d, m, *J* = 46.6 Hz); ¹³C NMR (acetone-d₆) 43.1 (s); ³¹P NMR (acetone-d₆) δ 27.37(m), 16.20 (m), 6.09 (m, t, *J*_{P—F} = 905 Hz); ¹⁹F NMR (acetone-d₆) δ -62.56 to -59.36 (d, t, *J*_{P—F} = 912 Hz); HRMS (EI) calc. 468.9738, found *m/e* 468.9733.

X-RAY MEASUREMENT SECTION

Single-crystal X-ray Diffraction Analysis of 3,3,5,5-bis-spiro(N,N'-dinitroethylenediamino)-1,1-difluorocyclotriphosphazene quarter hydrate.

C₄H₈F₂N₁₁O₈P₃·1/4(H₂O), F.W. = 473.1, triclinic space group P(-1), *a* = 12.013(2), *b* = 14.541(2), *c* = 20.278(3) Å, α = 104.46(2), β = 100.89(2), γ = 99.38(2)°, *V* = 3284.9(8) Å³, *Z* = 8, ρ_{calc} = 1.913 mg mm⁻³, 1(Mo Kα) = 0.71073 Å, μ = 0.455 mm⁻¹, F(000) = 1904, *T* = 294°K.

A clear colorless 0.10 × 0.35 × 0.55 mm crystal, in the shape of a thick plate, was used for data collection on an automated Seimens R3m/V diffractometer equipped with an incident beam monochromator. Lattice parameters were determined from 25 centered reflections within 30° × 2θ × 40°. The data collection range of *hkl* was: -12 ≤ *h* ≤ 12, -15 ≤ *K* ≤ 15, 0 ≤ *l* ≤ 21, with [(sin θ)/λ]_{max} = 0.538. Three standards, monitored after 97 reflections, exhibited random variations with devs. up to

$\pm 2.0\%$ during data collection. A set of 8928 reflections was collected in the $\theta/2\theta$ scan mode, with scan width $[2\theta(K_{\alpha 1}) - 1.0]$ to $[2\theta(K_{\alpha 2}) + 1.0]^\circ$ and a constant ω scan rate of $15.63^\circ/\text{min}$. There were 8632 unique reflections, and 6673 were observed with $F_0 > 3\sigma(F_0)$. The data were corrected for Lorentz and Polarization effects and a semi-empirical absorption correction was applied, maximum and minimum transmission, 0.86 and 0.75 respectively. The structure was solved and refined with the aid of the SHELXTL system of programs.¹¹ The full-matrix least-squares refinement varied 1020 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms, and one common isotropic thermal parameter for all of the hydrogen atoms. Fixed H atoms were included on the methylene carbon atoms by using a riding model [coordinate shifts of C applied to attached H atoms, C—H distances set to 0.96 Å, H angles idealized].

Final residuals were $R = 0.040$ and $wR = 0.040$ with final difference Fourier excursions of 0.36 and -0.28e Å^{-3} . The water oxygen atom is strongly indicated in a difference Fourier map at a peak density of 3.74e Å^{-3} , and its omission would raise the R values to $R = 0.059$, and $wR = 0.077$. No hydrogen atoms were located on the water molecule.

Supplementary Material Available: Tables of atomic coordinates, bond distances and angles will be submitted to the Cambridge Structural Database, and are also available from the author (RG).

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