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The X-ray Structure Determinations and Semiempirical PM3 Calculations of Two Chloro(piperidyl)cyclotri(phosphazenes)[#]

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ABSTRACT

*Single crystals of 2,4,6,6-tetrachloro-2,4-bis(piperidyl)cyclotri(phosphazene) (***1a***) and of 2,4,6-trichloro-2,4,6-tris(piperidyl)cyclotri(phosphazene) (***2a***) were grown from petroleum ether solution. The structures of both compounds were determined by single-crystal X-ray diffraction analyses. Compound* **1a** *crystallizes in the monoclinic space group* $P\,2_1/n$ *with* $Z = 4$ *and unit cell dimensions* $a = 9.3994(4)$, $b = 19.204(3)$, $c = 11.5664(4)$ Å, *and* $\beta = 108.718(4)°$. *Compound* **2a** *crystallizes in the triclinic space group* $P\,\bar{1}$ *with* $Z = 4$ *and unit cell dimensions* $a = 12.8289(2)$, $b = 13.8856(2)$, $c = 14.63810(10)$ Å, *and* $\alpha = 100.7621(5)$, $\beta = 91.0094(2)$, $\gamma = 113.9757(6)°$. *The experimentally obtained structural parameters for the covalent molecules* **1a** *and* **2a** *compare well with those calculated at the semiempirical PM3 level of theory. These results give credence to the PM3 calculated structures of 2,4,6,6-tetraazido-2,4-bis(piperidyl)cyclotri(phosphazene) (***1b***) and 2,4,6-triazido-2,4,6-tris(piperidyl)cyclotri(phosphazene) (***2b***) for which presently there are no experimental data available.*[†] *© 1997 John Wiley & Sons, Inc. Heteroatom Chem* **8***: 267–271, 1997.*

INTRODUCTION

We have recently been studying the reactions of trimeric phosphorus nitrile chloride, $[PNCl_2]_3$, toward silver azide, sodium azide, and activated sodium azide [1–3]. Phosphorus nitrile azide, $[PN(N_3)_2]_3$, which can be isolated in pure form, was first prepared by Grundmann and Rätz in 1955 [4] and is one of the most nitrogen-rich inorganic compounds. This material is extremely shock sensitive in the solid state with almost no kinetic stabilization and therefore of no use for any practical application as a primary explosive [2]. However, organic derivatives of phosphorus nitrile chloride of the type $P_3N_3Cl_{6-n}R_n$ ($n = 1, 2, \ldots, 5$) that have one to five chlorine atoms substituted by organic groups R (cf. earlier work [5] and related studies by Ahmed and Fortier [6]) represent interesting precursors for the preparation of kinetically more stabilized phosphorus nitrile azide derivatives of the type $P_3N_3(N_3)_{6-n}R_n$ ($n = 1, 2, \ldots, 5$). In our research group, we are pres-

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[#] Prior to publication the results presented in this paper were made available to the DRA (UK).

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[†] Non-SI units employed: 1 kcal ≈ 4.184 kJ, 1 Å = 10^{-10} m (since these units are still used in computational chemistry, we employed them throughout the article).

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ently exploring the chemistry of piperidyl substituted cyclotriphosphazenes (i.e., R = NC_5H_{10}). It is often difficult to grow single crystals suitable for X-ray diffraction studies of the azido derivatives. On the other hand, for the practical use of primary explosives, the azido compounds are required as powdered samples (not as crystalline material), and so the lack of a strong tendency of crystallization is not necessarily a disadvantage [7]. However, to get some detailed information about the molecular structures of these compounds, we decided to calculate the structures of the isolated covalent molecules at the semiempirical PM3 level of theory. Since the azide group can be regarded as a pseudohalogen [8], and the group electronegativity (χ) of the N_3 radical was calculated to lie between the value for Cl and that for Br (χ values in eV: Cl 8.3, Br 7.5, N_3 7.7 [9,10]), it is reasonable to assume that the molecular properties of $P_3N_3(N_3)_{6-n}R_n$ compounds will be similar to those of their chlorine analogues $P_3N_3Cl_{6-n}R_n$. In the work presented in this article, we therefore chose the Cl compounds $P_3N_3Cl_4(NC_5H_{10})_2$ (**1a**) and $P_3N_3Cl_3(NC_5H_{10})_3$ (**2a**), which can easily be obtained in crystalline form, to determine their structures by X-ray diffraction methods and by semiempirical PM3 calculations. We then planned to focus on the computed structures of the azido derivatives $P_3N_3(N_3)_4(NC_5H_{10})_2$ (**1b**) and $P_3N_3(N_3)_3(NC_5H_{10})_3$ (**2b**) for which there are presently no experimental data available.

EXPERIMENTAL

Materials and Methods

Single crystals suitable for X-ray diffraction analysis of compounds **1a** and **2a** were grown by slow evaporation of saturated solutions of these compounds in petroleum ether at 18°C.

The triazido and tetraazido derivatives **1b** and **2b** were prepared from reactions of **1a** and **2a** with activated sodium azide in aqueous acetone and were isolated by extraction with diethyl ether following the literature procedure for the preparation of hexaazidophosphazene [1,4].

Correct C/H/N analyses were obtained for compounds **1a**, **2a**, and **2b** (compound **1b** was for safety reasons not subjected to an elemental analysis).

All compounds (**1a**–**2b**) show only one very broad resonance in the ^{14}N NMR (14.462 MHz, PW = 48 μs, 5000 scans, 20°C) spectrum in CH_2Cl_2/acetone solution between −200 and −400 ppm.

X-Ray Structure Determination for Compound 1a

Crystal Data. 2,4,6,6-Tetrachloro-2,4-bis(piperidyl)cyclotri(phosphazene) (**1a**), $P_3Cl_4N_5C_{10}H_{20}$, M = 445.03, monoclinic, a = 9.3994(4), b = 19.204(3), c = 11.5664(4) Å, and β = 108.718(4)°; V = 1977.4(3) $Å^{-3}$, space group P $2_1/n$, Z = 4, D_c = 1.495 g cm^{-1}. Crystal dimensions 0.30 × 0.30 × 0.35 mm, $\mu(\text{Cu-}K_\alpha)$ = 7.77 mm^{-1}, λ = 1.5418 Å, $F(000)$ = 923.02.

Data Collection and Processing. Rigaku AFC6S diffractometer, 20°C, $\theta/2\theta$ scan mode, $2\theta_{max}$ = 120.0°, graphite monochromated Cu-K_α radiation, 2889 independent measured reflections, 1615 observed [$I_{net} > 2.5\ \sigma\ I_{net}$]. Absorption corrections were made.

Structure Analysis and Refinement. The structure was solved by direct methods, and all nonhydrogen atoms were refined anisotropically. Refinement was by full-matrix least squares to R_F = 0.060 ($R_F = \Sigma[F_0 - F_c]/\Sigma[F_0]$), R_w = 0.061 (R_w = Sqrt. $[\Sigma\{w[F_0 - F_c]^2\}/\Sigma\{wF_0^2\}]$); for all reflections: R_F = 0.128, R_w = 0.066. In the last D-map, the deepest hole was −0.46 e $Å^{-3}$, and the highest peak was 0.41 e $Å^{-3}$. Computations were carried out using the NRCVAX program system and published scattering factors [11–13].

X-ray Structure Determination for Compound 2a

Crystal Data. 2,4,6-Trichloro-2,4,6-tris(piperidyl)cyclotri(phosphazene) (**2a**), $P_3Cl_3N_6C_{15}H_{30}$, M = 493.72, triclinic, a = 12.8289(2), b = 13.8856(2), c = 14.63810(10) Å, α = 100.7621(5), β = 91.0094(2), γ = 113.9757(6)°; V = 2327.96(5) $Å^{-3}$, space group P $\bar{1}$, Z = 4, D_c = 1.409 g cm^{-1}. Crystal dimensions

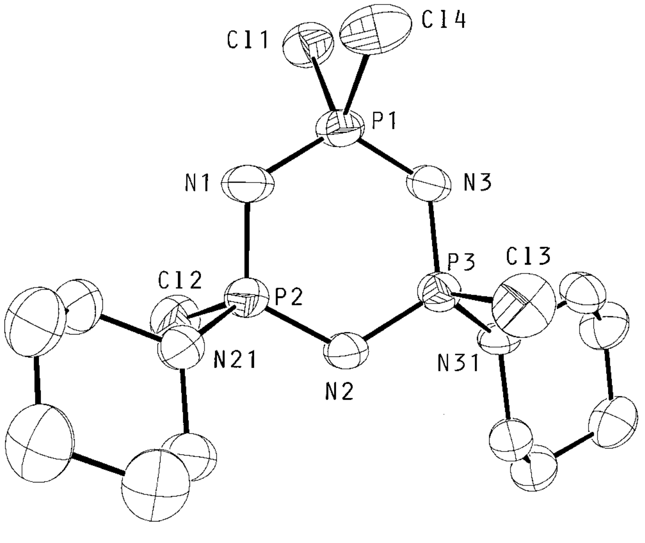

FIGURE 1 Molecular structure of **1a** in the crystal (ORTEP representation).

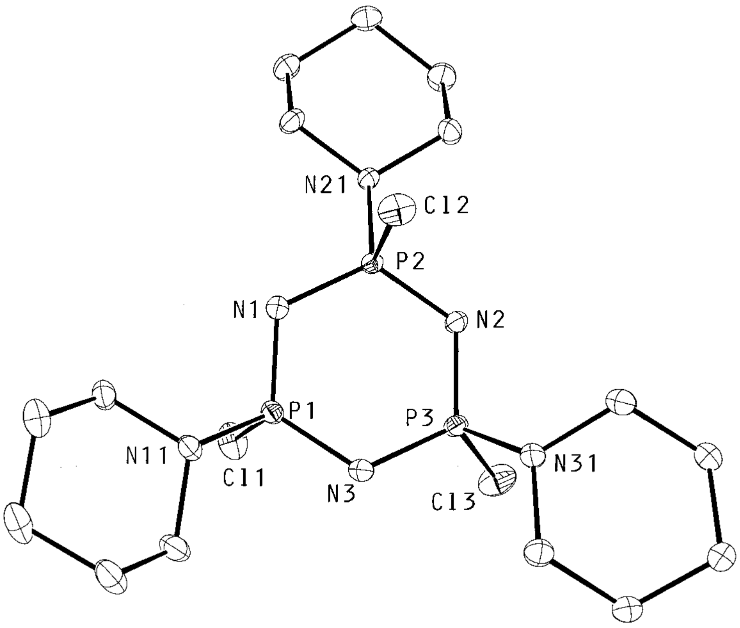

FIGURE 2 Molecular structure of **2a** in the crystal (ORTEP representation).

TABLE 1 Selected Measured (X-ray) and Computed (PM3) Bond Lengths (Å) and Angles (°) for Compounds **1a** and **2a**[a]

	*X-ray (**1a**)*	*PM3 (**1a**)*	*X-ray (**2a**)*	*PM3 (**2a**)*
P1-N3	1.568(6)	1.638	1.5803(14)	1.660
N3-P3	1.590(5)	1.663	1.5839(15)	1.662
P3-N2	1.572(5)	1.656	1.5755(17)	1.654
N2-P2	1.582(6)	1.662	1.5807(15)	1.661
P2-N1	1.588(6)	1.664	1.5851(16)	1.656
N1-P1	1.565(6)	1.635	1.5826(16)	1.662
P1-C11	1.987(3)	2.032	2.0639(7)	2.074
P1-C14	2.001(3)	2.032	—	—
P2-C12	2.052(4)	2.053	2.0524(7)	2.064
P3-C13	2.049(3)	2.085	2.0615(7)	2.079
P1-N11	—	—	1.6347(15)	1.747
P2-N21	1.603(6)	1.735	1.6290(15)	1.745
P3-N31	1.605(6)	1.742	1.6292(14)	1.747
C11-P1-C14	100.29(12)	99.2	—	—
Cl1-P1-N11	—	—	103.95(6)	102.1
Cl2-P2-N21	105.8(3)	103.8	105.05(6)	99.7
Cl3-P3-N31	105.7(2)	102.3	104.44(6)	101.9
P1-N3-P3	118.8(3)	126.6	119.54(10)	126.4
N3-P3-N2	117.9(3)	111.2	119.03(8)	112.4
P3-N2-P2	120.3(3)	127.2	120.87(10)	127.7
N2-P2-N1	118.3(3)	111.1	118.98(8)	112.0
P2-N1-P1	120.3(4)	127.4	120.02(9)	127.1
N1-P1-N3	119.3(3)	113.7	118.53(8)	112.8
N1-P1-N3-P3	−20.91(9)	−20.7	−18.3(4)	−12.0
N1-P2-N2-P3	1.48(9)	−1.6	−5.5(4)	2.6
N2-P3-N3-P1	14.93(9)	14.4	25.9(4)	7.7
N3-P1-N1-P2	17.22(9)	15.0	−1.5(3)	−11.1

[a] Atomic labeling for the PM3 structures in analogy to Figures 1 and 2.

0.15 × 0.20 × 0.40 mm, $\mu(\text{Mo-}K_\alpha) = 0.61\ \text{mm}^{-1}$, $\lambda = 0.71073$ Å, $F(000) = 1031.81$.

Data Collection and Processing. Siemens SMART diffractometer using a CCD detector, −150°C, $2\theta_{\text{max}} = 57.5°$, graphite monochromated Mo-K_α radiation, 11,922 independent measured reflections, 9654 observed [$I_{\text{net}} > 2.5\ \sigma\ I_{\text{net}}$]. No correction was made for absorption.

Structure Analysis and Refinement. The structure was solved by direct methods, and all nonhydrogen atoms were refined anisotropically. Refinement was by full-matrix least squares to $R_F = 0.033$ ($R_F = \Sigma[F_0 - F_c]/\Sigma[F_0]$), $R_w = 0.043$ ($R_w = \text{Sqrt}.[\Sigma\{w[F_0 - F_c]^2\}/\Sigma\{wF_0^2\}]$); for all reflections, $R_F = 0.045$, $R_w = 0.045$. In the last D-map, the deepest hole was -0.52 e Å^{-3}, and the highest peak was 0.92 e Å^{-3}. Computations were carried out using the NRCVAX program system and published scattering factors [11–13].

Further details of the crystal structure determinations are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-59386, the names of the authors, and the journal citation.

Semiempirical PM3 Computations. All calculations were carried out with the program package HyperChem [14] at the semiempirical PM3 [15] level

TABLE 2 Computed (PM3) Energies and Selected Bond Lengths (Å) and Angles (°) for Compounds **1b** and **2b**[a]

	*PM3 (***1b***)*	*PM3 (***2b***)*
E^{PM3} (kcal mol^{-1})[b]	−4734	−5956
P1-N3	1.658	1.668
N3-P3	1.665	1.669
P3-N2	1.674	1.685
N2-P2	1.669	1.674
P2-N1	1.678	1.663
N1-P1	1.655	1.680
P1-N1a	1.777	1.772
N1a-N1b	1.236	1.238
N1b-N1c	1.129	1.131
P1-N4a	1.742	—
N4a-N4b	1.246	—
N4b-N4c	1.127	—
P2-N2a	1.768	1.781
N2a-N2b	1.238	1.234
N2b-N2c	1.128	1.131
P3-N3a	1.793	1.772
N3a-N3b	1.229	1.235
N3b-N3c	1.132	1.130
P1-N11	—	1.753
P2-N21	1.753	1.763
P3-N31	1.749	1.760
N1a-P1-N4a	97.8	—
N1a-P1-N11	—	102.5
N2a-P2-N21	103.9	100.8
N3a-P3-N31	04.9	103.6
P1-N3-P3	125.2	125.3
N3-P3-N2	113.9	113.7
P3-N2-P2	124.8	124.6
N2-P2-N1	112.7	112.1
P2-N1-P1	127.0	124.4
N1-P1-N3	113.8	113.1
N1a-N1b-N1c	173.5	171.8
N2a-N2b-N2c	172.0	172.4
N3a-N3b-N3c	173.1	172.1
N4a-N4b-N4c	171.6	—
N1-P1-N3-P3	−3.8	14.1
N1-P2-N2-P3	11.5	−24.5
N2-P3-N2-P1	15.2	−10.6
N3-P1-N1-P2	−5.5	−24.1

[a] Atomic labeling for the PM3 structures of **1b** and **2b** in analogy to Figures 1 and 2 (the Cl1, Cl2, Cl3, and Cl4 atoms of compounds **1a** and **2a** have been replaced by the azide N atoms N1a, N1b, N1c; N2a, ..., N4c.

[b] The PM3 energies for **1a** and **2a** are E^{PM3} (**1a**) = −3837 kcal mol^{-1} and E^{PM3} (**2a**) = −5289 kcal mol^{-1}.

of theory using a VSTO-3G* basis set. We chose PM3 (which differs from AM1 [16] only in the values of the parameters) since the parameters for PM3 were derived by comparing a much larger number and wider variety of experimental versus computed molecular properties. The PM3 is a reparameterization of AM1, which is based on the neglect of diatomic differential overlap (NDDO) approximation. NDDO retains all one-center differential overlap terms when Coulomb and exchange integrals are computed.

RESULTS AND DISCUSSION

The molecular structures of compounds **1a** and **2a** were determined experimentally by X-ray diffraction analysis and computed at the semiempirical PM3 level of theory. Figures 1 and 2 show the molecular structure of **1a** and **2a** [17] determined by X-ray diffraction. Table 1 summarizes the most important experimentally obtained and calculated structural parameters for compounds **1a** and **2a**.

Generally, the calculated and observed structural parameters for **1a** and **2a** are in good agreement. Both molecules were calculated and found to exist in a slight chair conformation (cf. torsion angles in Table 1; cf. also related molecules [6]). In both cases, all calculated bond angles nicely reflect the observed trend (within ±5°). The PM3 calculation always seems to predict somewhat too long bond lengths (0.075 Å for the P–N distances within the six-membered ring system, 0.03 Å for the P–Cl bonds, and 0.1 Å for the exocyclic P–N bonds). These results give credence to the calculated structural parameters for those related molecules for which there are presently no experimental data available. The PM3 calculated structures and energies of 2,4,6,6-tetraazido-2,4-bis(piperidyl)cyclotri(phosphazene) (**1b**) and 2,4,6-triazido-2,4,6-tris(piperidyl)cyclotri(phosphazene) (**2b**) are summarized in Table 2. As expected, **1b** and **2b** also exist in a slight chair conformation with the azide groups slightly bent (172–174°) as one would expect for a covalently bound N_3 unit [2].

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[17] Note that there are two unique molecules in the unit cell of **2a**.