Heteroatom Chemistry
Volume 8, Number 3, 1997

The X-ray Structure Determination and Semiempirical PM3 Calculations of 2,4,4,6,6-Pentachloro-2-(piperidyl)cyclotri(phosphazene)

David Adam, Thomas M. Klapötke,* and Axel Schulz

University of Glasgow, Department of Chemistry, Glasgow G12 8QQ (UK), Telefax: Int. code + (141) 330 4199; E-mail: tmk@chem.gla.ac.uk

Received 16 December 1996

ABSTRACT

*The structure of 2,4,4,6,6-pentachloro-2-(piperidyl)-cyclotri(phosphazene) (**1**) was determined by single-crystal X-ray diffraction analysis. Compound **1** crystallizes in the orthorhombic space group P_{bea} with Z = 8 and unit cell dimensions a = 8.316(2), b = 17.261(3), and c = 22.007(4) Å. The experimentally obtained structural parameters for compound **1** compare well with those calculated at the semiempirical PM3 level of theory. These results give credence to the PM3-calculated structure of 2,4,4,6,6-pentaazido-2-(piperidyl)cyclotri(phosphazene) (**2**) for which presently there are no experimental data available.*[†] *© 1997 John Wiley & Sons, Inc. Heteroatom Chem **8**: 283–286, 1997.*

INTRODUCTION

Quite recently, we have reported in this journal on the experimental (X-ray) and PM3-computed structures of $P_3N_3Cl_4(NC_5H_{10})_2$ and $P_3N_3Cl_3(NC_5H_{10})_3$, as well as on computational studies of the corresponding azides $P_3N_3(N_3)_4(NC_5H_{10})_2$ and $P_3N_3(N_3)_3(NC_5H_{10})_3$ [1]. We were able to establish that the semiempirical PM3 level of theory is suitable to predict the structures of phosphazene derivatives in a very cpu time efficient way. We have now extended our studies to the pentachloro phosphazene derivative **1** and its azide analog **2**. For **2**, there are presently no experimental structural data available. In the work presented in this article, chose the Cl compound $P_3N_3Cl_5(NC_5H_{10})$ (1), which can easily be obtained in crystalline form, to determine the structure by X-ray diffraction methods and by semiempirical PM3 calculations. We then decided to focus on the computed structure of the azido derivative $P_3N_3(N_3)_5(NC_5H_{10})$ (**2**) for which there are presently no experimental data available.

EXPERIMENTAL

Materials and Methods

Single crystals of compound **1** (crystallized from petroleum ether) suitable for X-ray diffraction analysis were provided to us by Dr. Porte (see Acknowledgments). The pentaazido derivative **2** was prepared by the reaction of **1** with activated sodium azide in aqueous acetone and was isolated by extraction with diethyl ether following the literature procedure for the preparation of hexaazidophosphazene [2,3]. Correct C/H/N analyses were obtained for compound **1** (compound **2** was, for safety reasons, not subjected to an elemental analysis). Both compounds (**1** and **2**) show only one very broad resonance in the ^{14}N NMR (14.462 MHz, PW = 48 μs, 5000 scans, 20°C,)

---

*To whom correspondence should be addressed; LMU Munich, Inst. of Inorganic Chemistry, D-80333 Munich, Germany.

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

© 1997 John Wiley & Sons, Inc.
1042-7163/97/030283-04

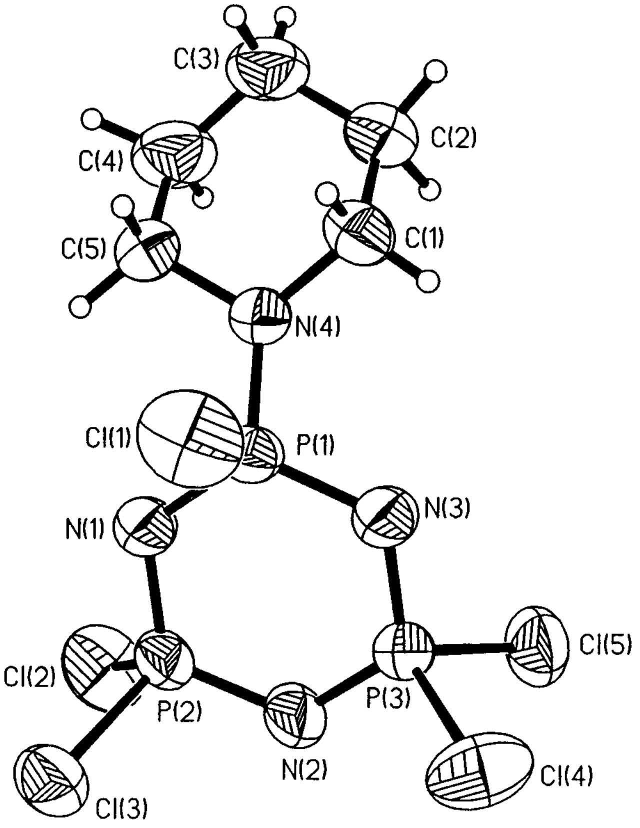

FIGURE 1 Molecular structure of **1** in the crystal (ORTEP representation).

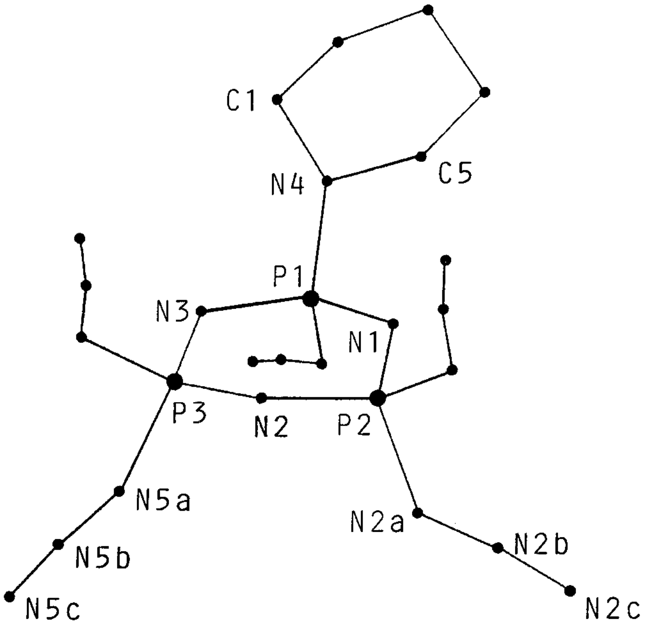

FIGURE 2 PM3-computed molecular structure of **2**.

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

(**1**)	*X-ray* (**1**)	*PM3* (**1**)	(**2**)	*PM3* (**2**)
Cl1-P1	2.033 (2)	2.051	N1a-P1	1.774
Cl3-P2	2.006 (2)	2.031	N3a-P2	1.746
Cl5-P3	2.006 (2)	2.027	N5a-P3	1.766
P1-N3	1.596 (4)	1.664	P1-N3	1.684
P2-N1	1.562 (3)	1.630	P2-N1	1.661
P3-N2	1.575 (4)	1.639	P3-N2	1.664
Cl2-P2	1.987 (2)	2.027	N2a-P2	1.766
Cl4-P3	2.000 (2)	2.030	N4a-P3	1.747
P1-N1	1.601 (4)	1.667	P1-N1	1.668
P1-N4	1.620 (3)	1.740	P1-N4	1.760
P2-N2	1.586 (3)	1.642	P2-N2	1.663
P3-N3	1.568 (3)	1.635	P3-N3	1.657
			N1a-N1b	1.240
			N1b-N1c	1.128
Cl1-P1-N1	106.4 (1)	107.5	N1a-P1-N1	110.2
Cl1-P1-N3	106.2 (2)	108.5	N1a-P1-N3	108.3
Cl1-P1-N4	106.4 (1)	100.7	N1a-P1-N4	100.9
N1-P1-N3	117.4 (2)	108.8	N1-P1-N3	111.0
N1-P1-N4	109.9 (2)	115.7	N1-P1-N4	113.2
N3-P1-N4	109.9 (2)	114.9	N3-P1-N4	112.6
Cl2-P2-Cl3	101.1 (7)	100.0	N2a-P2-N3a	98.9
Cl2-P2-N1	108.2 (1)	112.8	N2a-P2-N1	113.2
Cl2-P2-N2	109.0 (2)	111.1	N2a-P2-N2	115.0
Cl3-P2-N1	110.7 (1)	110.0	N3a-P2-N1	109.9
Cl3-P2-N2	107.1 (1)	110.8	N3a-P2-N2	108.0
N1-P2-N2	119.1 (2)	111.5	N1-P2-N2	111.0
Cl4-P3-Cl5	100.5 (1)	100.2	N4a-P3-N5a	98.5
Cl4-P3-N2	108.7 (2)	111.0	N4a-P3-N2	108.8
Cl4-P3-N3	109.7 (2)	109.4	N4a-P3-N3	111.4
Cl5-P3-N2	107.7 (1)	111.2	N5a-P3-N2	112.8
Cl5-P3-N3	109.4 (2)	112.4	N5a-P3-N3	113.1
N2-P3-N3	119.2 (2)	112.1	N2-P3-N3	111.5
P1-N1-P2	120.7 (2)	129.6	P1-N1-P2	124.8
P2-N2-P3	120.4 (2)	127.9	P2-N2-P3	124.4
P1-N3-P3	121.3 (3)	128.9	P1-N3-P3	124.2
P1-N4-C1	117.5 (3)	119.4	P1-N4-C1	117.4
P1-N4-C5	118.3 (2)	118.3	P1-N4-C5	119.6
			N1a-N1b-N1c	173.0
N3-P1-N1-P2	13.0 (3)	12.1	N3-P1-N1-P2	28.1
N4-P1-N1-P2	139.5 (2)	143.2	N4-P1-N1-P2	155.9
N1-P1-N3-P3	−9.3 (4)	−12.6	N1-P1-N3-P3	−27.6
N4-P1-N3-P3	−135.8 (2)	−144.2	N4-P1-N3-P3	−155.8
N2-P2-N1-P1	−14.4 (3)	−6.6	N2-P2-N1-P1	−29.3
N1-P2-N2-P3	11.9 (4)	0.2	N1-P2-N2-P3	30.5
N3-P3-N2-P2	−8.2 (4)	−0.3	N3-P3-N2-P2	−30.4
N2-P3-N3-P1	7.0 (4)	7.7	N2-P3-N3-P1	28.7
E^{PM3}/kcal mol^{-1}		−2384.0		−3514.3
zpe/kcal mol^{-1}		105.9		
NIMAG		0		0

[a] Atomic labeling for the PM3 structures in analogy to Figure 1; in the azide derivative, the Cl atoms Cl1, Cl2, . . . Cl5 are replaced by N1a, N1b, N1c, N2a, N2b, N2c, . . . N5a, N5b, N5c with Na bound to P, Nb being the central and Nc the terminal N atom.

spectrum in CH_2Cl_2/acetone solution between $\delta = -200$ and -400.

X-ray Structure Determination for Compound 1

Crystal Data. 2,4,4,6,6-Pentachloro-2-(piperidyl)cyclotri(phosphazene) (**1**), $P_3Cl_5N_4C_5H_{10}$, M =

396.35, orthorhombic. $a = 8.316(2)$, $b = 17.261(3)$, and $c = 22.007(4)$ Å: $V = 3159(1)$ Å^3, space group P_{bca}, $Z = 8$, $D_c = 1.667$ g cm^{-1}. Crystal dimensions $0.20 \times 0.20 \times 0.15$ mm, $\mu(\text{Mo-}K_\alpha) = 1.21$ mm^{-1}, $\lambda = 0.71069$ Å, $F(000) = 1584.0$.

Data Collection and Processing. Siemens P4 diffractometer, 20°C, $\theta/2\theta$ scan mode, $2\theta_{max} = 60.0°$, graphite monochromated Mo-K_α radiation, 4558 independent measured reflections, 3140 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 block-cascade full-matrix least squares to $R = 0.0608$, $R_w = 0.0871$ ($R_w = 1/[s^2(F_0^2) + (0.1300\ P) + 1.800\ P]$, where $P = (F_0^2 + 2\ F_c^2)/3$). Computations were carried out using the SHELXS-86 and SHELXL-93 program systems and published scattering factors [4–6].

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 numbers CSD-406341, the names of the authors, and the journal citation.

Semiempirical PM3 Computations. All calculations were carried out with the program package HyperChem [7] at the semiempirical PM3 [8] level of theory using a VSTO-3G* basis set. We chose PM3 (which differs from AM1 [9] only in the values of the parameters) since the parameters for PM3 were derived by comparing a much larger number and a wider variety of experimental versus computed molecular properties. The PM3 level of theory is a reparametrization 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 structural parameters of compound **1** were determined experimentally by X-ray diffraction analysis and computed at the semiempirical PM3 level of theory. Figure 1 shows the molecular structure of **1** determined by X-ray diffraction. Table 1 summarizes the most important experimentally obtained and calculated structural parameters for compounds **1** and **2**.

Generally, the calculated and observed structural parameters for compound **1** are in good agreement. Both molecules, the pentachloro (**1**) as well as the pentaazido derivative (**2**) were calculated to exist in a slight chair conformation (cf. torsion angles in Table 1; cf. also related molecules [10]). For compound **1**, 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 bond; cf. earlier work [1]). This result gives credence to the calculated structural parameters of compound **2** for which there are presently no experimental data available. The PM3-calculated structure and energies of 2,4,4,6,6-pentaazido-2-(piperidyl)cyclotri(phosphazene) (**2**) (Figure 2) are also summarized in Table 1. As expected, compound **2** also exists in a slight chair conformation with the azideo groups slightly bent (172–174°), as one would expect for a covalently bound N_3 unit [1,11].

ACKNOWLEDGMENTS

The authors thank Dr. Andrew L. Porte for supplying compound **1** and Dr. Peter S. White for many helpful discussions. This work was financially supported by the University of Glasgow and the North Atlantic Treaty Organization (NATO, CRG 920034-3 [TMK, PSW]).

REFERENCES

[1] T. M. Klapötke, P. S. White. *Heteroatom Chemistry, 8*, 1997, 267.

[2] P. Geissler, Diplomarbeit, TU Berlin, Berlin (1994).

[3] C. Grundmann, R. Rätz, *Z. Naturforsch., 10b,* 1955, 116.

[4] (a) G. M. Sheldrick, *SHELXS-86, Structure Solving Program for Crystal Structure Determination,* University of Göttingen, Germany (1986); (b) G. M. Sheldrick, *SHELXL-93, Program for the Refinement of Crystal Structures,* University of Göttingen, Germany (1993).

[5] *International Tables for X-ray Crystallography,* Kynoch, Birmingham vol. IV. (1974).

[6] (a) C. K. Johnson: ORTEP Plotting. *ORTEP—A Fortran Thermal Ellipsoid Plot Program,* Technical Report ORNL-5138 (1976); (b) S. Motherwell: Pluto Plotting, University Chemical Laboratory, Cambridge, U.K. (1978).

[7] HyperChem 4.0, Molecular Visualization and Simulation Program Package, Hypercube, Waterloo, Ontario (1994).

[8] (a) J. J. P. Stewart, *J. Comp. Chem., 10,* 1989, 209; (b) J. J. P. Stewart, *J. Comp. Chem., 10,* 1989, 221.

[9] (a) M. Dewar, W. Thiel, *J. Am. Chem. Soc., 99,* 1977, 4499; (b) M. J. S. Dewar, M. L. McKee, H. S. Rzepa, *J. Am. Chem. Soc., 100,* 1978, 3607; (c) M. J. S. Dewar,

E. G. Zoebisch, E. F. Healy, *J. Am. Chem. Soc., 107,* 1985, 3902; (d) M. J. S. Dewar, C. H. Reynolds, *J. Comp. Chem., 2,* 1986, 140.

[10] F. R. Ahmed, S. Fortier, *Acta. Cryst., B, 36,* 1980, 1456.

[11] I. C. Tornieporth-Oetting, T. M. Klapötke, *Angew. Chem. Int. Ed. Engl., 34,* 1995, 511.