ISSN 1063-7745, Crystallography Reports, 2010, Vol. 55, No. 7, pp. 1203–1206. © Pleiades Publishing, Inc., 2010.

STRUCTURE OF ORGANIC COMPOUNDS

Hexakis(4-phormylphenoxy)cyclotriphosphazene: X-ray and DFT-Calculated Structures[1]

Çiğdem Albayrak[a], Başak Koşar[a], Mustafa Odabaşoğlu[b], and Orhan Büyükgüngör[c]

[a] *Faculty of Education, Sinop University, Sinop, TR-57100, Turkey*
e-mail: calbayrak@sinop. edu.tr

[b] *Chemical Technology Program, Pamukkale University, TR-20159, Denizli, Turkey*

[c] *Faculty of Arts and Sciences, Ondokuz Mayis University, Samsun, TR-55139, Turkey*

Received December 14, 2009

Abstract—The crystal structure of hexakis(4-phormylphenoxy)cyclotriphosphazene is determined by using X-ray diffraction and then the molecular structure is investigated with density functional theory (DFT). X-Ray study shows that the title compound has C–H···π interaction with phosphazene ring. The molecules in the unit cell are packed with Van der Waals and dipole–dipole interactions and the molecules are packed in zigzag shaped. Optimized molecular geometry is calculated with DFT at B3LYP/6-311G(d,p) level. The results from both experimental and theoretical calculations are compared in this study.

DOI: 10.1134/S1063774510070175

INTRODUCTION

Hexachlorocyclotriphosphazene is an important compound because it is used in synthesis of most halophosphazene. Chlorine atoms attached to phosphorus atoms can easily replace with various nucleophiles to form different cyclotriphosphazene derivatives [1, 2]. Phosphazene-based compounds have been of interest due to a wide range of thermal and chemical stabilities [3–5]. Phosphazene compounds are important in industrial and medical fields. Some aminophosphazenes have antibacterial features [6, 7] and have shown activity against HIV virus [7]. They are advantageous for chemotherapeutic application because of their low toxicity [8].

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Synthesis

The compound hexakis(4-phormylphenoxy)cyclotriphosphazene was prepared by reflux a mixture of a solution containing 4-phormylphenoxide

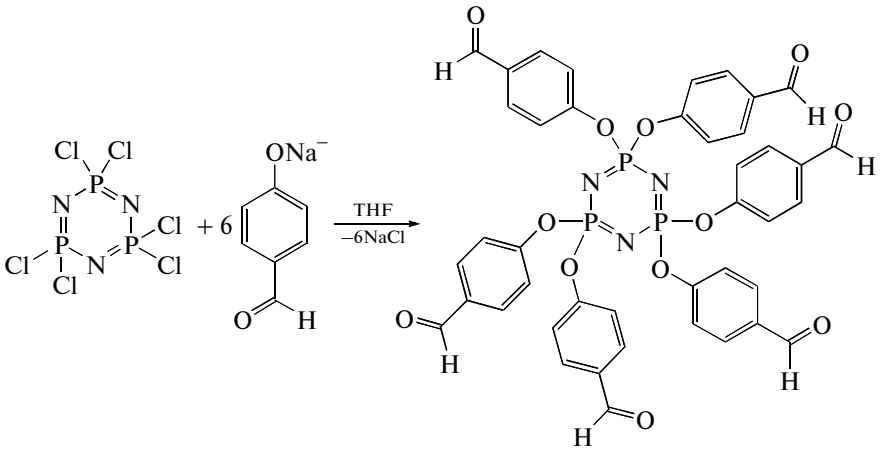

Fig. 1. The synthesis scheme of the title compound.

[1]The article is published in the original.

Table 1. Crystal data, data collection and refinement details

Chemical formula	$C_{42}H_{30}N_3O_{12}P_3$
Crystal System, Space group, Z	Orthorhombic, $P2_12_12_1$, 4
a, Å	7.8955 (3)
b, Å	14.1611 (5)
c, Å	35.3256 (18)
V, Å^3	3949.7 (3)
D_x, Mg m^{-3}	1.449
Radiation, λ	MoK_α, 0.71073 Å
μ, mm^{-1}	0.221
T, K	293
T_{min}, T_{max}	0.936, 0.990
F(000)	1776
Diffractometer	STOE IPDS II
Scanning mode	ω
Scan range	$-9 < h < 9$, $-17 < k < 17$, $-42 < l < 42$
θ_{min}, θ_{max}, deg	1.15, 25.66
Number of measured/independent reflections, R_{int}	28457/7467, 0.085
Number of reflections with $I > 2\sigma(I)$	3818
Number of refined parameters	543
S	0.849
$R[F^2 > 2\sigma(F^2)]$	0.052
$wR(F^2)$	0.108
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.36, −0.24

obtained by mixing metallic sodium (17.3 mmol, 0.39 g) in 50 ml dry THF and 4-hydroxybenzaldehyde (2.1 g, 17.3 mmol) and a solution containing hexachlorocyclotriphosphazene (1 g, 2.8 mmol) in 50 ml THF. The reaction mixture was stirred for 48 h under reflux. The crystals of hexakis(4-phormylphenoxy)cyclotriphosphazene suitable for X-ray analysis were obtained from acetonitrile by slow evaporation (yield % 71; m.p. 434–436 K) (Fig. 1).

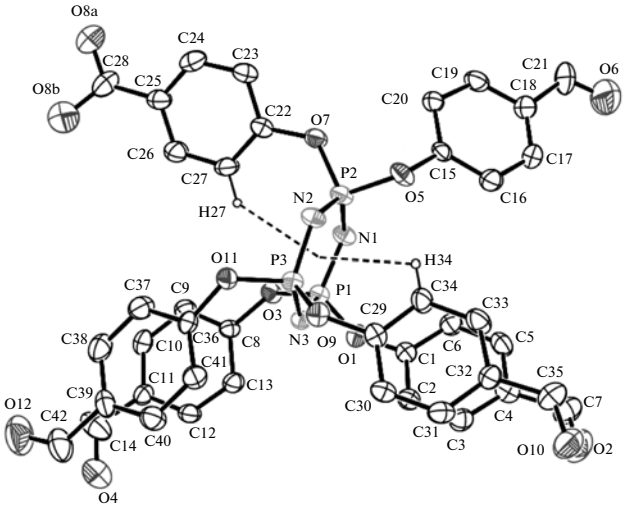

Fig. 2. An ORTEP-3 view of the title compound with the scheme. Dashed line shows Intramolecular C–H···π interactions.

X-Ray Diffraction Analysis

A suitable sample of size 0.50 × 0.24 × 0.06 mm was selected for the single crystal X-ray study. All diffraction measurements were performed using STOE IPDS 2 diffractometer. Reflections were collected in the rotation mode and cell parameters were determined by using X-AREA software [9]. Absorption correction was achieved by the integration method via X-RED software [9]. The structure was solved by direct methods using SHELXS97 [10]. The refinement was carried out by full-matrix least-squares method using SHELXL97 [10] on the positional and anisotropic temperature parameters of the non-hydrogen atoms, or equivalently corresponding to 543 crystallographic parameters. All H atoms were located in their idealized positions and refined using a riding model with C–H distances in the range 0.93 Å, U_{iso}(H) values in the range 1.2U_{cq}(C). The data collection conditions and parameters of refinement process are listed in Table 1.

CCDC 747368 contains the supplementary crystal lographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystal lographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Computational Procedure

The geometry optimization of the molecule leading to energy minima was achieved by using B3LYP hybrid exchange-correlation functional with 6-311G(d,p) basis set [11, 12]. The calculation was started from the crystallographically achieved atomic coordinates and carried out using GUSSIAN03W package [13]. The optimized molecular geometry, total molecular

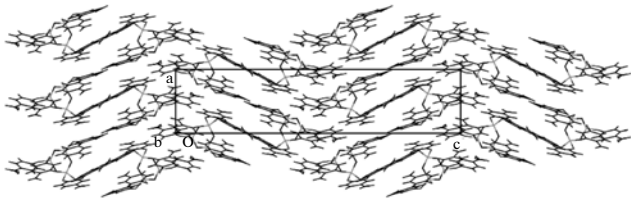

Fig. 3. A packing diagram of the title compound.

Table 2. Selected bond' lengths, angles and torsion angles (Å, deg)

	X-Ray	DFT/B3LYP		X-Ray	DFT/B3LYP
P1–N1	1.574(3)	1.5918	P1–O1	1.576(3)	1.617
P1–N3	1.575(3)	1.6018	P1–O3	1.590(3)	1.6119
P2–N1	1.573(3)	1.5992	P2–O5	1.577(3)	1.6076
P2–N2	1.571(4)	1.5924	P2–O7	1.571(3)	1.6185
P3–N2	1.568(4)	1.5918	P3–O9	1.580(3)	1.6109
P3–N3	1.587(3)	1.6035	P3–O11	1.569(3)	1.6115
O2–C7	1.143(9)	1.2088	O1–C1	1.392(6)	1.3941
O4–C14	1.216(9)	1.2091	O3–C8	1.392(6)	1.3923
O6–C21	1.133(11)	1.209	O5–C15	1.399(6)	1.3952
O8a–C28	1.169(13)	1.2088	O7–C22	1.383(7)	1.3946
O8b–C28	1.337	–	O9–C29	1.395(6)	1.3915
O10–C35	1.225(7)	1.2083	O11–C36	1.391(5)	1.3917
O12–C42	1.196(9)	1.2092	N1–P1–N3	117.08(18)	116.7444
P1–N1–P2	122.1(2)	122.5303	N1–P2–N2	117.8(2)	117.0136
P2–N2–P3	122.1(2)	123.3075	N2–P3–N3	117.75(19)	116.2476
P1–N3–P3	121.3(2)	121.8302	P1–O1–C1	120.7(2)	124.163
P1–O3–C8	126.7(3)	126.7187	P2–O5–C15	127.9(3)	125.9783
P2–O7–C22	128.0(3)	122.5479	P3–O9–C29	125.8(3)	126.6134
P3–O11–C36	123.7(3)	128.1924	P1–N1–P2–N2	2.7(4)	–0.3542
P3–N2–P2–N1	4.0(4)	1.6011	P2–N2–P3–N3	–0.4(4)	6.6783
P1–N3–P3–N2	–10.0(4)	–16.8673	P3–N3–P1–N1	16.2(4)	18.0898

energy, dipole moment, Mulliken charges were obtained from the computational process.

RESULTS AND DISCUSSION

An ORTEP-3 plot [14] with the atom-numbering scheme of the title compound is shown in Fig. 2 and selected bond distances and angles are listed Table 2. P–N bond lengths are 1.568–1.587 Å retaining their phosphazenic character. The results show that there are elongations of *Ar*–O bond lengths of this compound compared with the normal value for *Ar*–O bond length [15–17] and P–O bonds agree with their normal P–O bond length [18, 19].

The crystal structure is stabilized by C–H···π interactions with the phosphazene ring. The geometrical parameters of the intramolecular C–H···π interactions are listed in Table 3.

The packing of the molecules in the unit cell (Fig. 3) is due to van der Waals and dipole–dipole interactions. The molecules are packed in zigzag shaped.

In DFT/B3LYP calculations, total energy of optimized geometry and dipole moment of molecule are obtained as –3710.40927266 a.u. and 6.1429 D, respectively. According to calculated results for Mulliken atomic charge analysis, while atoms N1, N2, N3 and O1, O3, O5, O7, O9, O11 have larger negative charges relative to other atoms, atoms P1, P2, P3 have positive charges as expected. Charges are calculated as –0.794225, –0.793944, –0.830149, –0.540033, –0.517607, –0.531720, –0.534309, –0.527215, –0.525391, 1.321604, 1.328987, 1.322476, respectively.

Comparative results obtained from the X-ray crystallographic and computational studies of bond distances, angles and torsion angles are presented in Table 3. P–N and P–O bonds lengths in the X-ray structure are shorter than that of computational results. It is possible that unpaired electrons of oxygen atoms are shared partly by *d* orbitals of phosphorus atoms with d_π–p_π interaction. It is well known that the DFT and similar calculations underestimate interactions like inter- and intramolecular hydrogen bonds and handle molecules in gaseous phase (in vacuo). So, some differences were observed between X-ray experi-

Table 3. Hydrogen, bonding geometry (Å, deg)

D–H···*A*	*D*–H	H···*A*	*D*···*A*	∠*D*–H···*A*
C27–H27···*Cg*	0.93	2.7587	3.4191	128.79
C34–H34···*Cg*	0.93	2.9985	3.4992	115.36

Note: *Cg* is the centroid of P1–N1–P2–N2–P3–N3 ring.

mental study and DFT/B3LYP calculation results of bond distance, angle and torsion angle values.

REFERENCES

1. H. R. Allcock, P. E. Austin, and T. F. Rakowsky, Macromolecules (14), 1622 (1981).
2. M. Odabaşoğlu, G. Turgut, H. İçbudak, J. Mol. Struct. **691**, 249 (2004).
3. N. Lejeune, I. Dez, P. A. Jafferes, J. F. Lohier, P. J. Madec, J. Sopkova de Ollvera Santos, Eur. J. Inorg. Chem. **1**, 138 (2008).
4. D. Kumar, G. M. Fohlen, and J. A. Parker, Macromolecules **16** (8), 1250 (1983).
5. D. Kumar, M. Kuhullar, and A. D. Gupta. Polimer **34** (14), 3025 (1993).
6. C. F. Laberre, O. J. Bovin, and J. Goly, Acta Crystallogr. B **35**, 1182 (1979).
7. K. Brandt, R. Kruszynoki, T. J. Bartzak, and L. P. Czomperlik, Inorg. Chim. Acta **322**, 138 (2001).
8. H. Beak, Y. Cho, C. Lee, and Y. Shon, Anti Cancer Drugs **11**, 715 (2000).
9. Stoe & Circumstance, *X-AREA* (Version 1.18) and X-RED32 (Version 1.04) (Darmstadt, Germany, 2002).
10. G. M. Sheldrick, *SHELXS 97 and SHELXL 97, Program for Crystal Structure Solution and Refinement* (University of Göttingen, Göottingen, Germany, 1997).
11. C. Lee, W. Yang, and R. G. Part, Phys. Rev. B: Condensed Matter **37**, 785 (1988).
12. A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
13. M. D. Frisch et al., *GAUSSIAN03W. Revision E.01* (Gaussian Inc., Walfingford, CT, 2004).
14. L. J. Farrugia, *ORTEP-3 for Windows* (Dept. of Chemistry, University of Glasgow, Glasgow, 1998).
15. A. Özek, Ç. Albayrak, M. Odabaşoğlu, O. Büyükgüngör Acta Crystallogr. C **63**, ol77, (2007).
16. N. Karadayi, Ç. Albayrak, M. Odabaşoğlu, O. Büyükgüngör, Acta Crystallogr. E **62**, ol699 (2006).
17. N. Karadayi, Ç. Albayrak, M. Odabaşoğlu, O. Büyükgüngör, Acta Crystallogr. E **62**, ol727 (2006).
18. M. Odabaşoğlu, O. Büyükgüngör, Ç. Albayrak. Acta Crystallogr. E **61**, o2525 (2005).
19. M. Odabaşoğlu, O. Büyükgüngör, and Ç. Albayrak, Acta Crystallogr. E **61**, e4 (2005).