ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 6, pp. 1065–1068. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © E.M. Chistyakov, S.N. Filatov, V.V. Kireev, K.A. Lysenko, M.I. Buzin, V.P. Chuev, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 6, pp. 906–909.

Synthesis and Structure of Hexa-*p*-acetamidophenoxycyclotriphosphazene

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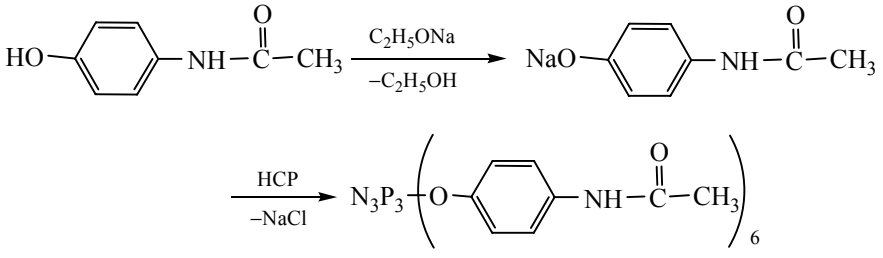
Received March 30, 2011

Abstract—Hexa-*p*-acetamidophenoxycyclotriphosphazene was synthesized and examined by the ^{31}P and ^{1}H NMR spectroscopy and XRD analysis.

DOI: 10.1134/S1070363212060047

One of the important trends in chemistry is the study of supramolecular structures organized on a nano-level. Due to their structure and functionality as well as the possibility to vary their properties by the chemical modification, cyclophosphazenes, in particular hexachlorocyclotriphosphazenes are an interesting object of both theoretical and experimental supramolecular chemistry. Starting from phosphazenes self-organizing structures were obtained with a desired shape and geometry based on electrostatic interactions, hydrogen or coordination bonding [1–3]. Starting from cyclophosphazenes a series of compounds capable of forming the clathrates was also synthesized [4–7]. The formation of supramolecular ensembles in these clathrates occurs via the immobilization of the small molecules in the lattices of macromolecular compounds. The formed compounds can be widely used, for example, in the manufacture of matrices for polymerization reactions, to separate the molecules in the preparation of compounds with nonlinear optical activity, to purify drugs, to capture and store toxic substances. The presence in the crystal lattice of hexa-*p*-acetamidophenoxycyclotriphosphazene of large cavities capable to form clathrate compounds makes them promising for scientific and applied research.

The synthesis of hexa-*p*-acetamidophenoxycyclotriphosphazene (HCP) was performed by the phenolate method as follows.



HCP = Hexachlorocyclotriphosphazene.

During the reaction all the chlorine atoms in the triphosphazene ring can be replaced with a minimal probability of side-reactions. The phenolates were obtained in the reaction of phenol with sodium ethoxide.

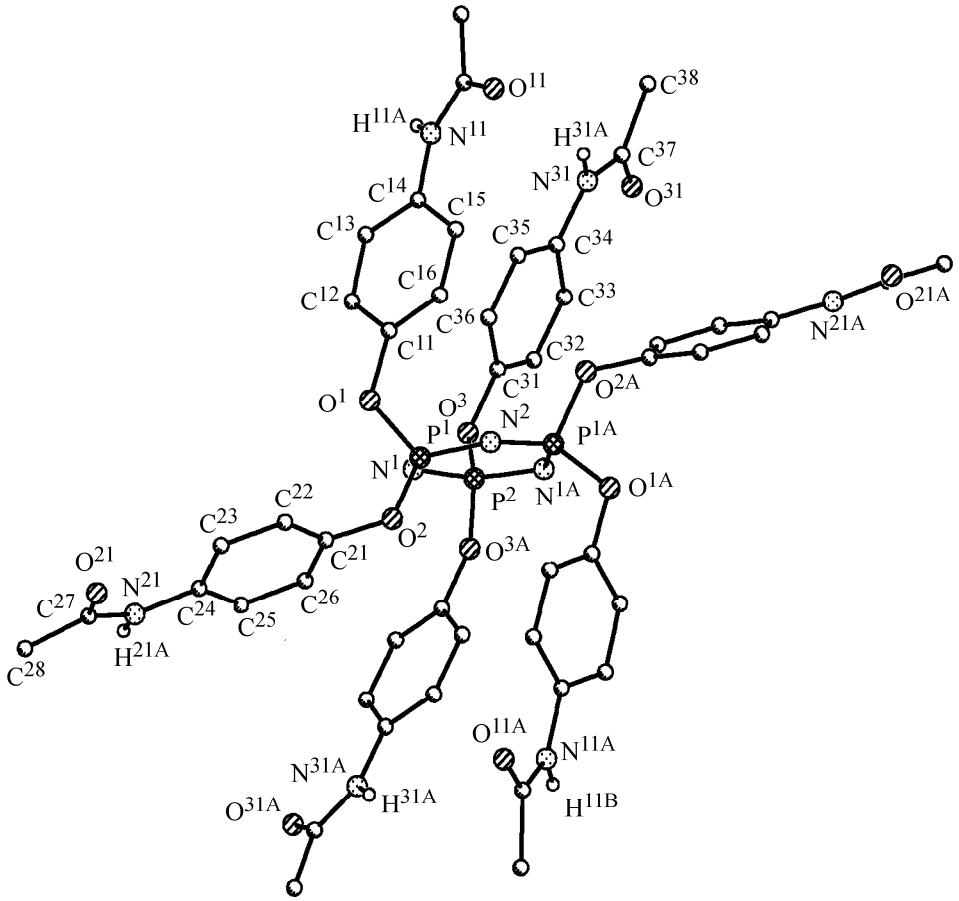


Fig. 1. General view of hexa-*p*-acetamidophenoxycyclotriphosphazene by the X-ray data.

Hexa-*p*-acetamidophenoxycyclotriphosphazene is a crystalline substance. According to the XRD analysis, the conformation of the phosphazene ring is a *semi-chair*. The P^1 and N^2 atoms are out-of-plane by 0.22 and 0.14 Å (the standard deviation does not exceed 0.01 Å, Fig. 1). The main bond lengths and the bond angles are given in Tables 1 and 2, respectively.

Analysis of the crystal packing showed that the molecules are bonded by the sufficiently strong N–H···O bonds with the distance between the proton donor and acceptor in the range of 2.732(3)–2.965(3) Å. The molecules are cross-linked by these bonds into a three-dimensional framework (Fig. 2a), where sufficiently large channels 14×15 Å have been identified directed along the crystallographic axis. During the crystallization of hexa-*p*-acetamidophenoxycyclotriphosphazene from THF these channels are able to be filled with six solvent molecules (Fig. 2b).

The TGA curve for the recrystallized sample of the obtained phosphazene has a stepwise character (Fig. 3). In the low-temperature range of 100–125°C the sample mass loss is 7% due to the crystal solvate destruction and THF removal. On recrystallization, a very stable complex between the hexa-*p*-acetamidophenoxy-

Table 1. Bond lengths in the hexa-*p*-acetamidophenoxycyclotriphosphazene molecule

Bond	Length, Å	Bond	Length, Å
P^1–N^2	1.577(3)	P^1–O^1	1.583(3)
P^1–O^2	1.581(3)	P^2–N^1	1.577(4)
P^1–N^1	1.580(5)	P^2–O^3	1.589(4)

Table 2. Bond angles in the hexa-*p*-acetamidophenoxycyclotriphosphazene molecule

Angle	ω, deg	Angle	ω, deg
$N^2P^1O^2$	106.56(18)	$N^{1A}P^2N^1$	116.7(3)
$N^2P^1N^1$	117.3(3)	$N^{1A}P^2O^3$	110.35(17)
$O^2P^1N^1$	112.3(2)	$N^1P^2O^3$	111.25(18)
$N^2P^1O^1$	110.4(2)	$N^1P^2O^{3A}$	110.35(17)
$O^2P^1O^1$	99.25(17)	$O^3P^2O^{3A}$	94.8(3)
$N^1P^1O^1$	109.5(2)	$P^2N^1P^1$	122.6(2)
$P^{1A}N^2P^1$	122.1(4)		

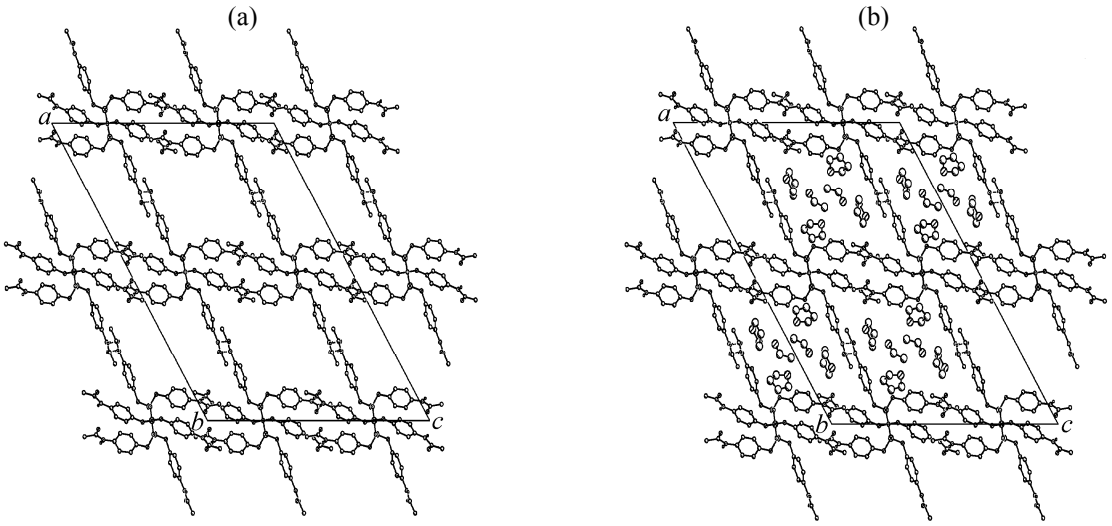


Fig. 2. Fragment of the crystal packing of hexa-*p*-acetamidophenoxycyclotriphosphazene: (a) N–H···O hydrogen bonding and (b) a solvate with THF molecules.

cyclophosphazene and the solvent in an equimolar ratio is formed. The product formed after the solvent removal is thermally stable up to 325°C.

Some thermal effects appear on the DSC curve of the recrystallized sample of hexa-*p*-acetamidophenoxycyclophosphazene at the first heating (Fig. 4, curve *1*). The first, endothermic, effect at 99°C (ΔH 6.31 J g^{-1}) corresponds to the removal of the solvent molecules. The second, exothermic, effect occurs in the temperature range of 120–170°C and is associated with the recrystallization of the fragments of the cyclotriphosphazene crystal lattice broken in the solvent removing process (ΔH 7.18 J g^{-1}). Finally, the third, endothermic, peak with a maximum at 260°C corresponds to the crystalline phase melting (ΔH 80.6 J g^{-1}). On cooling with a rate of 20 deg min^{-1} the sample remains amorphous. The DSC curve (Fig. 4, curve *2*) contains only a change in a heat capacity of the sample at the glass transition point. The DSC termogram of reheating the hexa-*p*-acetamidophenoxycyclotriphosphazene (Fig. 4, curve *3*) contains a heat capacity jump at the devitrification of the amorphous phase (T_v 113°C) and successive exo- and endothermal effects corresponding to the formation and melting of the crystal phase. On re-heating the heats of the cold crystallization and melting of hexa-*p*-acetamidophenoxycyclotriphosphazene are similar and equal to 54.5 J g^{-1}. The melting point (the maximum endothermic peak at 257°C) is slightly lower than that observed during the first heating of the sample. Thus, the crystallization from the melt in a DSC experiment leads to the formation of more defective crystalline phase than during the crystallization from solution.

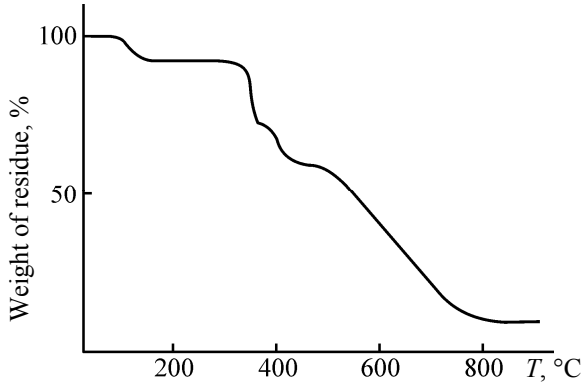


Fig. 3. TGA curve of hexa-*p*-acetamidophenoxycyclotriphosphazene at heating in air with a rate of 10 deg min^{-1}.

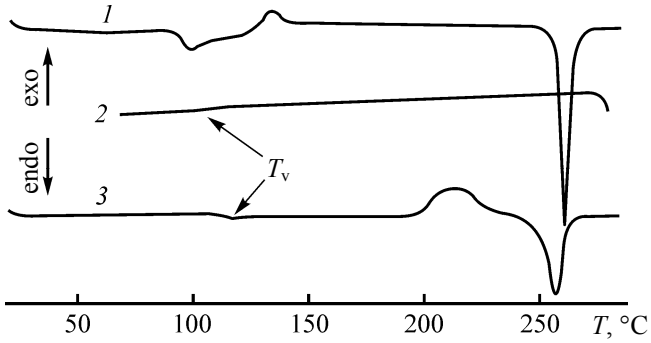


Fig. 4. DSC curve of hexa-*p*-acetamidophenoxycyclotriphosphazene at the first (*1*), the second (*3*) heating and cooling (*2*). The heating/cooling rate is 20 deg min^{-1} in argon atmosphere.

EXPERIMENTAL

4-Acetamidophenol (paracetamol, 98%, Acros), sodium metal (pure, Reachim, Czechia), phosphorus pentachloride (98%, Acros), ammonium chloride (of chemical grade, Laverna), petroleum ether 40–70 (LLC "Khimvest"), 2-methoxyethyl ether (99%, Acros), pyridine (of analytical grade, LLC "Khimvest") were used without further purification. Benzene (of analytical grade, "Khimmed") was dried over calcium chloride and distilled. Tetrahydrofuran and dioxane (BASF) were kept over alkali, then dried and distilled over metallic sodium. Ethyl alcohol (96.5%, Glavspirt) was dried over aluminum amalgam and distilled. The ^{31}P and ^{1}H NMR spectra were registered on a Bruker CXP-200 spectrometer in a DMSO-d_6 solution. The X-ray diffraction analysis was performed on a SMART APEX II CCD diffractometer (MoK_α-irradiation, graphite monochromator, ω-scanning). The structure was solved by the direct methods and refined by a full-matrix anisotropic approximation F^2_{hkl}.

The thermogravimetric study (TGA) was performed on a Derivatograph-C instrument (MOM, Hungary) for the sample of ~10 mg in air at a heating rate of 10 deg min^{-1}.

The differential scanning calorimetry (DSC) was performed on a DSC-822e calorimeter (Mettler-Toledo, Switzerland) for the sample of ~10 mg at a rate of heating/cooling of 20 deg min^{-1} in an argon atmosphere. The transition temperatures were determined by the minimum/maximum peak position on the DSC-termogram.

Hexachlorocyclotriphosphazene was obtained by ammonolysis of phosphorus pentachloride with ammonium chloride in pyridine [8]. Chlorophosphazenes were extracted with benzene, the higher cyclic products were separated by precipitation with petroleum ether and purified by the repeated recrystallization of hexachlorocyclotriphosphazene from heptane, mp 113°C. ^{31}P NMR spectrum (50.3 MHz, $CDCl_3$): δ_P 19.8 ppm.

Synthesis of hexa-*p*-acetamidophenoxycyclo-triphosphazene. Into a 3-neck flask equipped with a stirrer and reflux condenser was placed 7.9 g (0.06 mol) of *p*-acetamidophenol and 30 ml of ethanol. After the complete dissolution of *p*-acetamidophenol a solution of sodium ethoxide [prepared by dissolving 1.15 g (0.05 mol) of sodium in 20 ml of ethanol] was added with stirring. The reaction was carried out over 10 min, after which ethanol was distilled off on a vacuum rotary evaporator. The resulting phenolate was dried in a vacuum to the constant mass.

Into a 3-neck flask equipped with a stirrer and reflux condenser were placed 10.38 g (0.06 mol) of paracetamol phenolate and 40 ml of 2-methoxyethyl ether. In parallel, a solution of 2.61 g (0.0075 mol) of hexachlorotriphosphazene in 20 ml of 2-methoxyethyl ether was prepared, which was poured into the reaction flask with stirring. The reaction was performed over 9 h in a boiling solvent, and then the reaction mixture was filtered. The resulting solution was evaporated on a vacuum rotary evaporator. The product was purified by the recrystallization from THF. Yield 60%, mp 260°C. ^{1}H NMR [200 MHz, $(CD_3)_2SO$], δ, ppm: 1.98 s (CH_3), 6.74 d (H^m_{Ar}), 7.37 d (H^o_{Ar}), 9.88 s (NH). ^{31}P NMR spectrum [81.0 MHz, $(CD_3)_2SO$]: δ_P 10.43 ppm.

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