Russian Journal of General Chemistry, Vol. 75, No. 3, 2005, pp. 381–385. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 3, 2005, pp. 417–421.

Synthesis and Properties of Onium Salts of Isocyanuric Acid. Crystal Structure of Tetraphenylphosphonium Isocyanurate

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Received July 9, 2003

Abstract — Previously unknown tetrabutylammonium and tetraphenylphosphonium isocyanurates were prepared, and their IR spectra were examined. The crystal structure of tetraphenylphosphonium isocyanurate was determined.

The supramolecular chemistry, an actively developing field of science [1, 2], is based on weak intermolecular interactions such as coordination and hydrogen bonding, van der Waals interactions, and π–π overlap. The capability of isocyanuric acid (1,3,5-triazine-2,4,6-trione, **I**) and its anions to form supramolecular structures is determined by their capability for hydrogen bonding.

Isocyanuric acid is of interest in view of the possibility of preparing hydrogen-bonded polymeric anions, which can be used as components of conducting organic compounds. Isocyanuric acid is weak and forms mono-, di-, and trisubstituted salts with various metals [3, 4]. Mono- and disubstituted salts are formed most readily, whereas preparation of trisubstituted salts requires a large excess of a strong alkali. Numerous inorganic salts of isocyanuric acid have been reported; however, isocyanurates of organic and heteroorganic cations are unknown.

Our goals were to prepare two onium salts of isocyanuric acid, tetrabutylammonium isocyanurate **II** and tetraphenylphosphonium isocyanurate **III**, to study their spectra, and to determine the crystal structure of **III**.

Cyanuric acid exhibits keto–enol tautomerism; the free acid in the crystals exists in the keto form (isocyanuric acid) [5], and in its coordination compounds the coordination occurs via N rather than O atom [6]. Monosubstituted isocyanurates of alkali and alkaline-earth metals are prepared by treatment of the acid with excess metal hydroxide [7–9]. Isocyanurates of other metals, including transition metals (Cd, Mn, Co, Cu, Ni), are prepared from sodium or potassium isocyanurate [10–12].

Organic and heteroorganic (onium) salts of isocyanuric acid can be prepared either by the reaction with an alkylammonium hydroxide, similarly to inorganic salts, or by the exchange of a monosubstituted inorganic salt with tetraalkylphosphonium bromide or chloride. Onium salts crystallize from water in the form of crystal hydrates of the approximate composition $PPh_4^+(C_3H_2N_3O_3)^- \cdot 3H_2O$, readiily soluble in organic solvents. The crystal hydrates lose water on recrystallization from absolute solvents. However, the anhydrous salts take up moisture in air. Therefore, the IR spectra of the anhydrous salts, recorded without special precautions, are virtually identical to those of the crystal hydrates.

The main characteristic vibration frequencies of salts **II** and **III**, isocyanuric acid, and its monosubstituted Na and K salts [3, 7] are given in Table 1. The characteristic frequencies of isocyanuric acid [13–17] at 1450–1600 cm^{-1}, correspond to the stretching vibrations ν(C–N) + ν(C=N) of the conjugated system of the *s*-triazine ring; the bending modes of this ring give bands at 784–810 cm^{-1}. The C=O stretching vibrations are manifested at 1695–1720 cm^{-1}, and ν(NH) vibrations of the ring amide groups, at 2828–2907 cm^{-1}. The spectra of the onium salts obtained resemble both the spectrum of the acid and the spectra of monosubstituted alkali metal isocyanurates, suggesting the presence of the $(C_3H_2N_3O_3)^-$ ion [18].

The differences in the characteristic frequencies in the spectra of the onium salts are associated with changes in the intermolecular interactions in the crystals, caused by incorporation of bulky organic or heteroorganic cations. Furthermore, in contrast to the inorganic salts, the cationic moiety also contributes to the spectrum. The spectra of **II** and **III** are largely similar, with the following differences. In the spectrum of **II**, compared to that of **III**, the C=N stretching band is split, the ranges of the stretching frequencies of the ring and C–N bonds are broader (by 34 and

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Table 1. IR spectra of isocyanuric acid and its salts, ν, cm^{-1}

Vibration type	Compound **I**	Monosubstituted Na and K salts of **I**	Compound **II**	Compound **III**
ν(NH) + hydrogen bond	3445, 3117, 3024, 2850, 2781	3490–2700	3536, 3449, 3144, 3041, 2959, 2874, 2840	3426, 3141, 3055, 2965, 2813
ν(C=O)	1778, 1724	1740, 1710	1740, 1712	1739, 1710
ν(C=N)	1680, 1645	1691, 1652, 1629	1676	
$\nu(C_3N_3)$	1589, 1471	1600, 1480, 1440	1598, 1485, 1416	1587, 1558, 1484, 1439
ν(C–N)	1399	1390–1350	1383, 1325	1385, 1357
δ(NH)	1226	1260–1221	1247	1246
ν(C–O)	1054	1090–1030	1166, 1109, 1086, 1069, 1032	1160, 1107, 1072, 1023
$\delta(C_3N_3)$	875	990–835	992, 922, 882, 845	997, 877
π(C=O)	774	790–710	789, 738, 707	794, 760, 723
δ(C=O)	537	565–535	557, 530	550, 528
δ(NCO)	460	480–420	476	470

30 cm^{-1}, respectively), and the $\delta(C_3N_3)$ and π(C=O) bands are shifted to lower frequencies. As in the inorganic salts, the NH vibration frequencies depend on the cation.

As compared to the acid, the existence of the anion in the enol form becomes more probable. As a result, the C=O sretching bands shift toward lower frequencies (from 1778 and 1724 to 1740 and 1710 cm^{-1}), characteristic of conjugated carboxamide groups, and a C=N stretching band appears at 1690–1630 cm^{-1}. The splitting and broadening of the ν(C–O), δ(C=O), and π(C=O) bands and the shift of the δ(NH) band relative to the initial acid are caused by the arising nonequivalence of the intramolecular and intermolecular bonds in the salts.

The crystal structure of **III** was refined in space group *P*1. The structure consists of two independent Ph_4P^+ cations (a and b) related by the symmetry pseudo-center in the point ~(0.5, 0.5, 0.5) and four independent, randomly disordered isocyanurate anions: two mutually overlapping anions (c and e) related by the symmetry pseudo-center in the point ~(0, 0, 0) and two mutually overlapping anions (d and f) related by the symmetry pseudo-center in the point ~(0, 0.5, 0). The initial occupancies of all the atoms of these anions were taken as 0.5. Then the occupancies *o*(c), *o*(d), *o*(e), and *o*(f) were refined by the least-squares method (along with the other structural parameters) assuming that *o*(c) = *o*(d) and *o*(e) = *o*(f) = 1 – *o*(c) = 1 – *o*(d).

In the least-squares refinement of this pseudo-centrosymmetrical structure of **III**, relatively soft equality conditions of the SADI type [19] were imposed on all the structurally equivalent bonds and interatomic distances. The results of this refinement are given in the Experimental. We obtained the following total occupancies of the atoms of the randomly disordered isocyanurate anions: *o*(c) = *o*(d) = 0.817(2) and *o*(e) = *o*(f) = 0.183(2).

The molecular-ionic structure of **III** in the crystal is shown in Figs. 1 and 2. Two independent Ph_4P^+ cations (a and b) have a usual structure and similar geometries. The P–C bond lengths are within 1.788(2)–1.801(2) Å. The average value, 1.795(5) Å, almost concides with the mean (for C_3–P^+–C_{Ar} fragments) P–C bond length, 1.793(11) Å [20]. The CPC bond angles in these cations are within 108.2(1)°–111.2(1)°, and the average value, 109.47°, is precisely equal to the tetrahedral angle.

In the crystal structure of **III**, the randomly disordered isocyanurate anions (c, d, e, f) are planar to within ±[0.004(2)–0.028(10)] Å (for the nine nonhydrogen atoms). Within the experimental error, these anions have the C_{2v} local symmetry with the twofold axis passing through the O^3, C^3, and N^3 atoms (the atom numbering is the same as in Figs. 1 and 2; here and in Table 2, indices c, d, e, and f at the atom numbers are omitted for brevity). The mean bond lengths and angles in the isocyanurate anions in **III** (Table 2) are typical of these anions [4].

In the crystal structure of **III**, the isocyanurate anions are linked in infinite (running along *b*-axis) chains by N–H···O=C hydrogen bonds. Each anion (c, d, e, f) is involved in four such H bonds (two from each side) (Figs. 1, 2). The interatomic distances and angles corresponding to these interanionic H bonds are as follows: N–H 0.86 and N···O 2.746(10)–2.787(3) Å

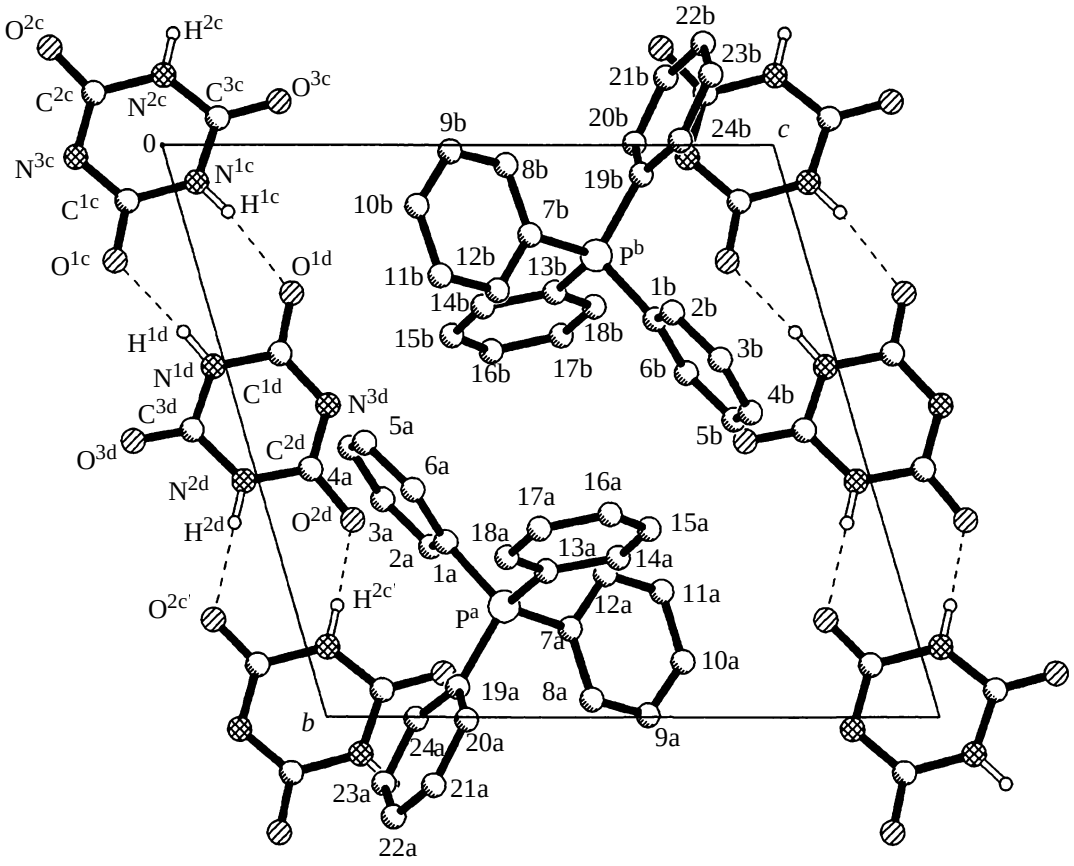

Fig. 1. Molecular-ionic structure of salt **III** in the crystal (projection along *x*-axis). The H atoms in Ph_4P^+ cations (a and b) and disordered cyanurate anions with low occupancies (e and f) are omitted for clarity.

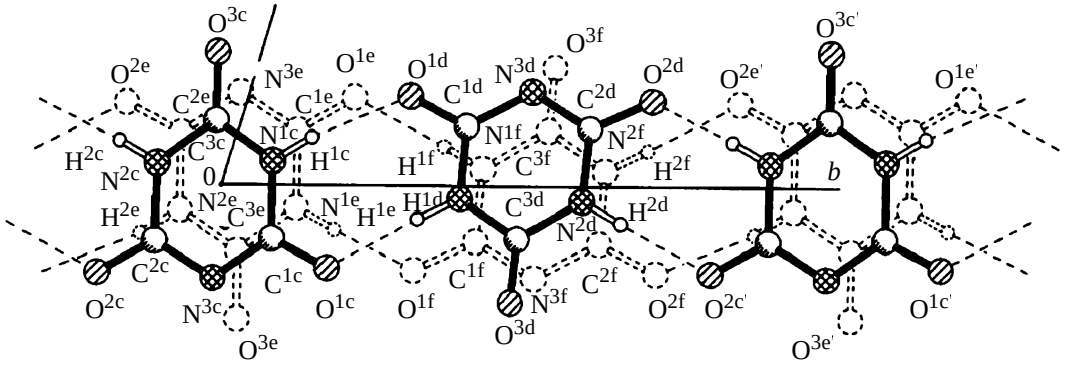

Fig. 2. Randomly disordered infinite chains ···c···d···c···d··· and ···e···f···e···f··· of randomly disordered isocyanurate anions c, d, e, and f in the crystal structure of **III** (projection along *x*-axis). The interanionic hydrogen bonds N–H···O=C are shown by dashed lines.

[average 2.77(1) Å], ∠(N–H···O) 161°–172° [average 167(3)°]. In all the isocyanurate anions, the O^3 and N^3 atoms are not involved in H bonds.

Since the isocyanurate anions are randomly disordered, the infinite H-bonded chains formed by them are also randomly disordered. Namely, the same place of the structure of **III** can be occupied with 81.7% probability by a chain of anions c and d and with 18.3% probability by a chain of anions e and f (Fig. 2).

There are no other H bonds in the crystal structure of **III**. All the other short interionic interatomic con-

Table 2. Average bond lengths (*d*) and average bond angles (ω) in the isocyanurate anions in **III**, taking into account the local symmetry (C_{2v}) of the anions

Bond	*d*, Å	Angle	ω, deg
$O^1{=}C^1$, $O^2{=}C^2$	1.243(2)	$C^1N^1C^3$, $C^2N^2C^3$	124.1(3)
$O^3{=}C^3$	1.216(2)	$C^1N^3C^2$	118.0(2)
$N^1{-}C^1$, $N^2{-}C^2$	1.383(2)	$O^1C^1N^1$, $O^2C^2N^2$	117.3(2)
$N^1{-}C^3$, $N^2{-}C^3$	1.363(3)	$O^1C^1N^3$, $O^2C^2N^3$	122.2(2)
$N^3{-}C^1$, $N^3{-}C^2$	1.338(2)	$N^1C^1N^3$, $N^2C^2N^3$	120.5(2)
		$O^3C^3N^1$, $O^3C^3N^2$	123.6(2)
		$N^1C^3N^2$	112.8(2)

tacts are close to, or slightly shorter than the sums of the corresponding van der Waals atomic radii. The cations are linked with anions by van der Waals and ionic interactions.

EXPERIMENTAL

Isocyanuric acid, tetraphenylphosphonium bromide, and tetrabutylammonium hydroxide (Aldrich) were used without additional purification. The IR spectra were recorded on a Perkin–Elmer-1720X Fourier spectrometer (KBr pellets).

Tetrabutylammonium isocyanurate II. Isocyanuric acid **I** (2.58 g) was dissolved in warm (60°C) EtOH, and 17.3 g of 30% aqueous solution of NBu_4OH (corresponds to 0.02 mol of anhydrous tetrabutylammonium hydroxide) was dissolved in EtOH. The solutions were combined and stirred at 60°C for 1 h. The solvent was removed on a rotary evaporator, and the residue was recrystallized from acetone. Salt **II** was obtained as fine neelde-like crystals. IR spectrum, ν, cm^{-1}: 3536, 3449, 3144, 3041, 2959, 2874, 2840, 1740, 1712, 1691, 1652, 1629, 1598, 1485, 1416, 1383, 1325, 1247, 1166, 1109, 1086, 1069, 1032, 992, 922, 882, 845, 789, 738, 707, 557, 530, 476. Found, %: C 61.3; H 10.9; N 15.4. $C_{19}H_{38}N_4O_3$. Calculated, %: C 61.6; H 10.3; N 15.1.

Tetraphenylphosphonium isocyanurate III. Isocyanuric acid **I** (2.58 g) was added to a hot solution of 1.12 g of KOH in 30 ml of water, and the solution was heated until the acid completely dissolved. The resulting solution was mixed with a solution of 8.38 g of tetraphenylphosphonium bromide in 20 ml of water and refluxed for ~1 h. The precipitate that formed on cooling was filtered off and recrystallized from water. The crystal hydrate of the approximate composition $PPh_4(C_3H_2N_3O_3)\cdot 3H_2O$ was obtained as long plates. Found, %: C 61.7; H 4.1; N 9.4. $C_{27}H_{28}N_3O_6P$. Calculated, %: C 62.2; H 5.4; N 8.1.

Anhydrous salt **III** was obtained by recrystallization of the crystal hydrate from absolute ethanol or chlorobenzene. Found, %: C 69.2; H 4.6; N 9.2. $C_{27}H_{22}N_3O_3P$. Calculated, %: C 69.4; H 4.7; N 9.0. Single crystals of **III** for X-ray diffraction study were obtained by recrystallization from chlorobenzene. IR spectrum, ν, cm^{-1}: 3426, 3141, 3055, 2965, 2813, 1739, 1710, 1676, 1587, 1558, 1484, 1439, 1385, 1357, 1246, 1160, 1107, 1072, 1023, 997, 877, 794, 760, 723, 699, 615, 550, 528, 470.

Single crystal X-ray diffraction study of III. The unit cell parameters of the crystals of **III** and the three-dimensional set of reflection intensities were obtained with an Enraf–Nonius CAD-4 autodiffractometer (MoK_α radiation, graphite monochromator). Crystals of **III** are triclinic; $(C_{24}H_{20}P)^+(C_3H_2N_3O_3)^-$, *M* 467.45; *a* 9.571(2), *b* 11.670(2), *c* 11.705(2) Å; α 73.34(2)°, β 86.25(2)°, γ 72.49(2)°; *V* 1194.1(4) $Å^3$; *Z* 2; d_{calc} 1.300 g cm^{-3}; μ(MoK_α) 0.149 mm^{-1}, space group *P*1.

The intensities of 7283 reflections were measured in the reciprocal space hemisphere ($2\theta \le 60°$), $\omega/2\theta$ scanning mode, crystal size $0.23 \times 0.39 \times 0.57$ mm. The intensities were measured in the special mode in which the final scanning was performed for all, including very weak, reflections.

The structure of **III** was solved by the direct method and refined by the full-matrix least-squares method on $F^2(hkl)$ in the approximation of anisotropic thermal vibrations of all nonhydrogen atoms (including disordered atoms). In the refinement, we used almost all the measured reflections [including very weak with $I < 2\sigma(I)$], except several reflections for which the measured and calculated F^2 values were poorly consistent.

In the crystal structure of **III**, the majority of the H atoms of two independent Ph_4P^+ cations were localized by the differential Fourier synthesis. Then the coordinates and individual isotropic thermal parameters of all the H atoms, including those of the disordered isocyanurate anions, were unambiguously calculated using the rider model [19] in the course of refinement of the structure of **III**. Using the least-squares method, we also refined the absolute structure parameter χ [21] and obtained the value of 0.56(11), indicating that the noncentrosymmetrical crystal is a racemic twin.

In the last cycle of the full-matrix refinement, the absolute shifts of all the 777 varied parameters of **III** were less than 0.001σ. The final refinement parameters [19] were as follows: R_1 0.037 and wR_2 0.098 for 6100 observed reflections with $I \ge 2\sigma(I)$; R_1 0.046

and wR_2 0.123 for all the 7283 measured unique reflections; goodness of fit S 1.03. In the final differential Fourier synthesis, $-0.17 < \Delta\rho < 0.24$ e Å^{-3}. The f curves and anomalous dispersion corrections to them ($\Delta f'$ and $\Delta f''$) were taken from the International Tables [22]. All the computations were performed with the SHELX-97 programs [19]. The atomic coordinates are filed at the Cambridge Structural Database.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 01-03-33 009).

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