Crystal packing of ammonium salts of arylenebis(phenylphosphinic) acids*

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> It was shown for the first time that the crystal packing mode of the ammonium salt of thiophene-2,5-diylbis(phenylphosphinic acid) substantially differs from that of the dimethylammonium salt of 1,4-phenylenebis(phenylphosphinic acid). The former crystal packing is a three-layer supramolecular sandwich structure consisting of two anionic layers separated by a layer of ammonium cations, whereas the supramolecular organization of the latter salt is based on alternating layers of anions and cations linked by hydrogen bonds.

> **Key words:** crystal engineering, supramolecular packing, X-ray diffraction study, phosphorus acids, ammonium salts.

The crystal engineering is a priority area of modern chemistry that is of high importance for the design of functional materials.¹ One of the basic principles of the construction of complex supramolecular systems is the molecular recognition of discrete molecules assembled to form highly ordered supramolecular architectures via various intermolecular interactions.² In this case, hydrogen bonds are of special importance because they are responsible for an additional binding in the crystal structures giving rise to supramolecular assemblies which can have different dimensionality, that is, they can be one-, two-, or three-dimensional (1D, 2D, or 3D, respectively). Hydrogen bonds are of particular importance for the construction of metal-organic coordination polymers (so-called metal-organic frameworks, MOF) in which the metal centers serve as units and are covalently linked to each other to form a particular substructure. The presence of hydrogen bonds is usually responsible for the formation of a porous structure of MOF, thus making them practically important.^{3,4}

Hence, the investigation of the structures of ammonium salts of organic acids is the first step toward the determination of the scope of the application of such systems for the construction of MOF and provides a deeper understanding of their structural potential, thus assisting in designing new materials.⁵ In addition, ammonium salts of organic and heteroorganic acids are of great interest for the design of practically important materials, such as proton-conductive membranes,^{6,7} hydrogen extraction devices,^{8,9} and highly sensitive sensors.^{10,11}

* Dedicated to Academician of the Russian Academy of Sciences A. I. Konovalov on the occasion of his 80th birthday. However, the scope of the application of phosphorus di- and polyacids in this area is not fully understood. Despite a considerable progress in studies of the structures and properties of ammonium salts of a number of phosphonic acids, such as benzylidenebisphosphonic acid, 1,4-phenylenebis(methylidene)tetrakis(phosphonic) acid,¹² and phosphonopropionic acid,¹³ ammonium derivatives of diphosphinic acids are virtually unknown, although the latter are characterized by the unique possibility of fine tuning the hydrophilic/hydrophobic balance.

In the present study, we report the synthesis of new arylenebis(phenylphosphinic acids) and the structures of ammonium salts on their basis.

Results and Discussion

Arylenebis(phenylphosphinic acids) were synthesized according to the method based on instability of the P-N bond in phosphorus acid amides to hydrolysis.

Thus, thiophene-2,5-diylbis(phenylphosphonous acid) diamide 1 undergoes hydrolysis to form acid 2 in a yield of about 63%. The slow diffusion of ammonia into a solution of acid 2 afforded crystals of salt 3 in quantitative yield (Scheme 1).

The similar reaction proceeding through amide 4 and acid 5 gave the dimethylammonium salt of 1,4-phenylenebis(phenylphosphinic acid) (6) (Scheme 2).

The supramolecular structure of these ammonium salts is determined by the main two factors: the nearly free rotation of phosphinate groups around P–C bonds (an aromatic bridging moiety) in anions and the ability of the ammonium cation to form hydrogen bonds. It should be noted that these factors are interrelated. The supra-

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 1, pp. 0182–0186, January, 2014.

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Scheme 1



i. 1) BuLi/TMEDA, 2) ClP(O)(NEt₂)Ph; ii. HCl/H₂O; iii. NH₃.

Scheme 2



i. 1) BuLi/TMEDA, 2) ClP(O)(NEt₂)Ph; ii. HCl/H₂O; iii. Me₂NH.

molecular structure of salt 3 is stabilized by the formation of intermolecular hydrogen bonds between the phosphinate moieties and the ammonium cations involving all four hydrogen atoms of the cations. Apparently, it is the presence of the unsubstituted ammonium cation that determines the conformation of the anion in the crystal. The phosphinate groups in the anion are located on one side of the thiophene group (Fig. 1). This orientation facilitates the formation of numerous hydrogen bonds between the cations and anions. Thus, each oxygen atom of the phosphinate group forms a bifurcated hydrogen bond with two ammonium cations which are, in turn, linked to the adjacent anion. Therefore, in the crystal, salt 3 forms a three-layer supramolecular sandwich structure consisting of two anionic layers separated by a layer of ammonium cations (Fig. 2). Adjacent anionic layers form a hydrophobic region with interpenetrating phenyl groups.

The supramolecular structure of salt **6** is radically different due apparently to the ability of the dimethylammonium cation to form only two hydrogen bonds, as opposed to the ammonium cation of salt **3**. The dimethylammonium cation links two phosphinate anions *via* hydrogen bonds and the anions, in turn, form hydrogen bonds with the cations involving all oxygen atoms. The structure of the anion in salt **6** fundamentally differs (see Fig. 1) from that in the crystal of compound **3**. Thus, the phosphinate groups are on the opposite sides of the benzene ring. Therefore, the anions serve as bridges between the layers consisting of cations and the supramolecular organization is based on alternating layers of anions and cations linked by hydrogen bonds (Fig. 3).

Therefore, the supramolecular organization of the ammonium salts of bisphosphinic acids provides evidence that the ability of anions and cations to form hydrogen bonds between each other and the conformational lability



Fig. 1. Structure and hydrogen bonding in the crystals of salts 3 (a) and 6 (b).



Fig. 2. Fragment of the crystal packing of salt 3.



Fig. 3. Fragment of the crystal packing of salt 6.

play a key role in these structures. The tetrahedral environment of the nitrogen atoms of the ammonium cations dictates the directionality of intermolecular interactions, whereas the number of hydrogen atoms in cations determines the number of intermolecular hydrogen bonds. It would be expected that such supramolecular organization can be observed for coordination compounds of bisphosphinic acids with metal ions which are prone to form complexes with a tetrahedral environment.

Experimental

All solvents were distilled over Na in the presence of benzophenone immediately before use. Methanol and ethanol of analytical grade were used as is without additional purification. The ¹H (400 MHz), ³¹P (161.975 MHz), and ¹³C (100.6 MHz) NMR spectra were recorded on a Bruker MSL-400 instrument using Me₄Si as the internal standard (¹H and ¹³C) and 85% H₃PO₄ as the external standard (³¹P) for 10% solutions in deuterated solvents (CDCl₃, DMSO-d₆). The IR spectra were measured on a Bruker Vector-22 FTIR spectrometer in the 400–4000 cm⁻¹ region at a 4 cm⁻¹ optical resolution in KBr pellets. The compound PhP(O)(Cl)(NEt₂) was synthesized according to a known procedure.¹⁴ The elemental analysis was carried out on a hightemperature Eurovector EuroEA3028-HT-OM CHNS-O elemental analyzer.

X-ray diffraction study. The X-ray diffraction data were collected at 150(2) K on a Bruker AXS Smart APEX diffractometer using Mo- $K\alpha$ ($\lambda = 0.71073$ Å; crystals of compound **3**) and Cu- $K\alpha$ radiation ($\lambda = 0.154184$ Å; crystals of compound **6**). The following programs were used: APEX2 (X-ray data collection),¹⁵ SAINT (data processing),¹⁶ SADABS version 2.10 (absorption correction),¹⁷ and SHELXS97 (structure solution).¹⁸ The structures were refined by the least-squares method using the SHELXL-97¹⁸ and WINGX-97 programs.¹⁹ The figures were generated using the ORTEP-3²⁰ and Mercury CSD 2.0 programs.²¹

All nonhydrogen atoms for both structures were refined anisotropically. The hydrogen atoms were positioned geometrically and refined using a riding model, except for the hydrogen atoms of the ammonium cations which were located in difference Fourier maps and refined isotropically.

Crystals of compound 3. Molecular formula $C_{16}H_{20}N_2O_4P_2S$, crystals dimensions $0.23 \times 0.2 \times 0.11$ mm³, M = 398.34, monoclinic, space group $P2_1/c$, a = 13.095(3) Å, b = 13.885(4) Å, c = 10.902(3) Å, $\alpha = \gamma = 90.00^{\circ}$, $\beta = 100.925(4)^{\circ}$, V = 1946.3(9) Å³, Z = 4, $\rho_{calc} = 1.359$ g cm⁻³, $\mu = 0.353$ mm⁻¹, $\theta_{max} = 28^{\circ}$, 23280 measured reflections, 4699 unique reflections ($R_{int} = 0.0751$), 3257 observed reflections ($I > 2\sigma(I)$), 258 refined parameters, $R_1 = 0.0441$, $wR_2 = 0.0934$ ($I > 2\sigma(I)$); residual electron density (max/min): 0.365/-0.349 e Å⁻³, GOOF = 1.013.

Crystals of compound 6. Molecular formula $C_{22}H_{30}N_2O_4P_2$, crystals dimensions $0.31 \times 0.25 \times 0.13$ mm³, M = 448.42, monoclinic, space group $P2_1/n$, a = 8.5720(10) Å, b = 6.5800(10) Å, c = 21.451(2) Å, $\alpha = \gamma = 90.00^{\circ}$, $\beta = 99.357(6)^{\circ}$, V = 1193.8(3) Å³, Z = 2, $\theta_{calc} = 1.247$ g cm⁻³, $\mu = 1.896$ mm⁻¹, $\theta_{max} = 63^{\circ}$, 17796 measured reflections, 1851 unique reflections ($R_{int} = 0.2224$), 1482 observed reflections ($I > 2\sigma(I)$), 152 refined parameters, $R_1 = 0.0893$, $wR_2 = 0.2166$ ($I > 2\sigma(I)$); residual electron density (max/min): 0.401/-0.903 e Å⁻³, GOOF = 1.019.

Synthesis of thiophene-2,5-diylbis(phenylphosphinic acid) (2). Tetramethylethylenediamine (TMEDA) (20 mL, 15.97 g, 132 mmol) was added to a solution of thiophene (4.75 mL, 5 g, 60 mmol) in petroleum ether (150 mL) under an inert atmosphere. Then a 1.6 Mn-butyllithium solution in hexane (82.51 mL, 131 mmol) was added dropwise under stirring. The reaction mixture was heated to 50 °C and kept at this temperature under stirring for 2 h. Then the reaction mixture was cooled to -78 °C, one-two drops of 15-crown-5 were added, and PhP(O)Cl(NEt₂) (28.34 g, 132 mmol) was added dropwise under stirring. Then the reaction mixture was gradually heated to room temperature and kept under stirring for 5 h. The resulting mixture was filtered and concentrated to a small volume. A solution of concentrated hydrochloric acid (25.3 mL, 291 mmol) in water (40 mL) was added under stirring to the precipitate. The reaction mixture was heated to 40 °C and kept at this temperature under stirring for 1 h. The precipitate that formed was filtered off. After the complete drying of the precipitate, thiophene-2,5-diylbis(phenylphosphinic acid) (2) was obtained in a yield of 13.78 g (63%) as a white powder with the melting point of 193 °C. ¹H NMR $(DMSO-d_6), \delta: 7.53 \text{ (m, 6 H, } m-, p-Ph); 7.58 \text{ (d, 2 H, } {}^3J_{PH} =$ = 6.67 Hz, C₄H₂S); 7.79 (ddd, 4 H, o-Ph, ${}^{3}J_{P,H}$ = 12.72 Hz, ${}^{3}J_{\text{H,H}} = 12.52 \text{ Hz}, \, {}^{4}J_{\text{H,H}} = 8.12 \text{ Hz}). \, {}^{31}\text{P NMR} \text{ (DMSO-d_6)},$ δ: 15.77. IR (KBr): 3432, 3071, 3018, 2996, 2983, 2923, 2852, 2622, 2588, 2518, 2458, 2141, 1965, 1669, 1596, 1569, 1498, 1439, 1333, 1309, 1294, 1274, 1217, 1181, 1132, 1098, 1039, 1001, 965, 833, 751, 720, 688, 576, 547, 494, 456. Found (%): C, 52.65; H, 3.97; P, 16.89; S, 8.56. C₁₆H₁₄O₄P₂S. Calculated (%): C, 52.75; H, 3.85; P, 17.03; S, 8.79.

Synthesis of diammonium thiophene-2,5-diylbis(phenylphosphinate) (3). Single crystals of salt 3 suitable for X-ray diffraction were obtained by the diffusion method. Liquid ammonia (0.3 mL) was added to a solution of thiophene-2,5-diylbis(phenylphosphinic acid) (0.03 g, 0.08 mmol) in THF (5 mL), and the mixture was allowed to stay for the slow diffusion. Transparent needle-like crystals formed on the walls of the tube in one day. The weight of the dry product was 0.033 g. The yield was 89%. Found (%): C, 48.03; H, 5.24; N, 6.50; P, 15.99; S, 8.06. $C_{16}H_{20}N_2O_4P_2S$. Calculated (%): C, 48.24; H, 5.03; N, 7.04; P, 15.58; S, 8.04.

Synthesis of 1,4-phenylenebis(phenylphosphinic acid) (5). A 1.6 M n-butyllithium solution in hexane (57.5 mL, 92 mmol, 5.91 g) was added dropwise under stirring under an inert atmosphere to a solution of 1,4-dibromobenzene (10 g, 42 mmol) in THF (150 mL) cooled to -78 °C. The reaction mixture was kept at this temperature under stirring for 4 h. Then one—two drops of 15-crown-5 were added, and a solution of PhP(O)Cl(NEt₂) (19.82 g, 92 mmol) in THF (25 mL) was added dropwise under stirring. Then the reaction mixture was gradually heated under stirring to room temperature and concentrated to a small volume. The precipitate that formed was filtered off. A solution of concentrated hydrochloric acid (16.0 mL, 184 mmol) in water (20 mL) was added under stirring to the filtrate. The reaction mixture was heated to 50 °C and kept at this temperature under stirring for 1 h. The resulting precipitate was filtered off. After the complete drying of the precipitate, 1,4-phenylenebis(phenylphosphinic acid) was obtained in a yield of 9.15 g (61%) as a white powder with the melting point of 330 °C. ¹H NMR $(DMSO-d_6), \delta: 7.47 (dd, 4 H, m-H_{Ph}, {}^3J_{H,H} = 7.40 Hz, {}^3J_{H,H} =$ $= 2.63 \text{ Hz}); 7.51 (d, 2 \text{ H}, p-\text{H}_{\text{Ph}}, {}^{3}J_{\text{H,H}} = 6.96 \text{ Hz}); 7.72 (dd, 4 \text{ H}, o-\text{H}_{\text{Ph}}, {}^{3}J_{\text{H,P}} = 11.77 \text{ Hz}, {}^{3}J_{\text{H,H}} = 6.93 \text{ Hz}); 7.80 (dd, 4 \text{ H}, C_{6}\text{H}_{4}, {}^{3}J_{\text{H,P}} = 9.08 \text{ Hz}, {}^{3}J_{\text{H,H}} = 5.66 \text{ Hz}). {}^{31}\text{P} \text{ NMR (DMSO-d_{6})}, \delta:$

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22.44. IR (KBr): 3434, 3058, 3026, 2962, 2929, 2855, 2606, 2266, 2162, 1685, 1593, 1486, 1438, 1384, 1338, 1314, 1262, 1193, 1161, 1135, 1071, 1023, 1001, 950, 826, 750, 718, 692, 587, 553, 487, 438. Found (%): C, 59.99; H, 4.57; P, 17.01. $C_{18}H_{16}O_4P_2$. Calculated (%): C, 60.34; H, 4.47; P, 17.32.

Synthesis of bis(dimethylammonium) 1,4-phenylenebis(phenylphosphinate) (6). Single crystals of $C_{22}H_{30}N_2O_4P_2$ suitable for X-ray diffraction were obtained by the diffusion method. An aqueous solution of dimethylamine was added to a solution of 1,4-phenylenebis(phenylphosphinic acid) (5) (0.03 g, 0.08 mmol) in a mixture of THF (4 mL) and water (1 mL), and the reaction mixture was allowed to stay for the slow diffusion. The weight of dry transparent needle-like crystals was 0.029 g. The yield was 87%. Found (%): C, 58.03; H, 6.97; N, 6.14; P, 13.89. $C_{22}H_{30}N_2O_4P_2$. Calculated (%): C, 58.93; H, 6.70; N, 6.25; P, 13.84.

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Received December 6, 2013; in revised form December 20, 2013