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Organoamino Phosphonium Cations as Building Blocks for Hierarchical Supramolecular Assemblies

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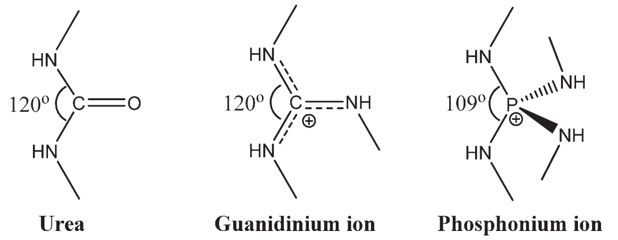
ABSTRACT: Organoamino phosphonium cations of formula $[P(NHR)_4]^+$ offer four hydrogen bonding sites that are arranged in tetrahedral fashion around the central phosphorus atom. This arrangement generates novel supramolecular building blocks that are distinct from the commonly planar NH donor systems, such as urea and guanidine. The supramolecular aggregation of these cations in the presence of chloride and several carboxylate anions is described. The carboxylate salts are obtained either by anion exchange reactions with phosphonium chlorides or by protonation reaction of the neutral phosphine imine $P(NPh)(NHPh)_3$. X-ray structure analyses of the title compounds show that they form hierarchical structures ranging from 1D chains to 2D sheets and 3D networks. Control over the dimensionality of the supramolecular structure can be achieved by modulating the steric bulk of the phosphonium cation.

Introduction

The design of new materials via crystal engineering has emerged as a major research topic over the past few decades.[1] While the main driving force for such approaches is to understand the supramolecular self-assembly process, the ultimate aim is to gain control over the supramolecular assembly process in order to produce designer crystals.[2] Several strategies have been developed to achieve this. For example, the network topology of metal−organic frameworks can be controlled to a great extent, which has enabled the synthesis of materials with specific properties.[3] As a result, metal−organic frameworks have shown enormous potential for applications ranging from host−guest chemistry and gas storage[4] to catalysis and sensors.[5] Thus the quest for new supramolecular building blocks that are able to generate structures of novel topologies and materials with certain properties, for example, metal-free organic frameworks, continues to grow at a steady rate.[6]

Phosphonium cations containing alkyl and aryl substituents play an important role in chemical synthesis, for example, the Wittig reaction.[7] They have been widely applied as phase transfer catalysts, such as in the ring-opening polymerization of epoxides.[8] These compounds also play an important role in many stereoselective syntheses. Chiral tetraaminophosphonium catalysts have been utilized in enantioselective transformations, for example, the Mannich reaction,[9] the Henry reaction, and the hydrophosphonylation of aldehydes.[10] Ooi and co-workers used an enantiopure tetraamino phosphonium phenoxide salt containing a spirocyclic cation as a supramolecular ion-pair catalyst in which the chiral information is transferred to the substrate via hydrogen bonding.[11] Recently, we showed that the organoamino-substituted phosphonium cation $[(PhNH)_4P]^+$ can be deprotonated to form anions that are valence-isoelectronic to PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$ ions.[12] Such ligands can offer binding sites for both Lewis acids and Lewis bases. For example, the monoanionic ligand $[(PhNH)_2P(NPh)_2]^-$, which is the N-analogue of the dihydrogen phosphate ion, contains a bidentate N−P−N site for the chelation of metal centers and a bidentate HN−P−NH site that can interact with anions via H-bonding.

Chart 1



Tetra(organoamino)phosphonium cations of the general formula $[P(NHR)_4]^+$ exhibit a tetrahedral arrangement of four RNH groups around the central phosphorus atom. As such they offer a unique coordination geometry for hydrogen bonding, which differs from that of the commonly planar NH donors such as urea and guanidinium (Chart 1).[13] The crystal structure of $[P(NHPh)_4]Cl$ shows that the $[P(NHPh)_4]^+$ ion binds two chloride ions via two HN−P−NH chelates, which are located at opposite sides of the cation and are twisted by 90° with respect to each other.[12a]

Spurred by the unique ligand geometry, we set out to explore the potential of these cations as supramolecular building blocks and the coordination modes of these cations in the presence of a range of anions. In particular, salts of anions containing carboxylate groups promise interesting structures, since these are potential double H-acceptors and thus compatible with the doubly H-donating HN−P−NH moiety of the cation. Carboxylic acids and carboxylic ions, especially those that contain several carboxylic groups, have been widely used as supramolecular synthons.[14] In addition, the steric and electronic properties of the $[P(NHR)_4]^+$ ion can be tuned via

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the modification of the four R-groups. Crystal structures of related organoamino phosphazenes and phosphazenium ions have shown that slight changes of R can have a profound effect on the dimensionality of the H-bonding network.[15]

Results and Discussion

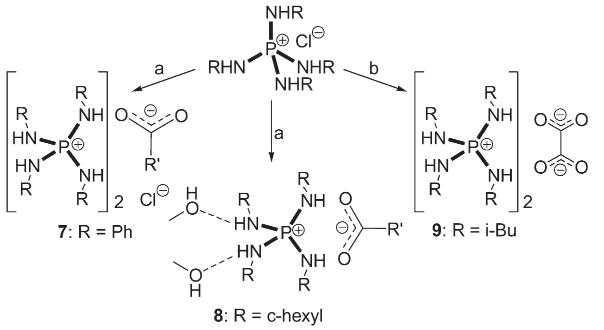
Synthesis. The chlorides [P(NHR)$_4$]Cl, **1** (R = phenyl), **2** (R = *n*-propyl), **3** (R = isopropyl), **4** (R = isobutyl), **5** (R = *tert*-butyl), and **6** (R = cyclohexyl), were prepared according to the literature procedure reported by Huheey and co-workers.[16] The crystal structures of **2**, **3**, **4**, **5**, and **6** were determined by X-ray crystallography and are discussed further below. The structure of **1** had been reported by us earlier.[12a] The chloride salts exchange anions when recrystallized from aqueous NaBr solutions. A crystal structure of the salt [P(NH^{n}Pr)$_4$]Br, **17**, was obtained.

Two routes have been employed to generate carboxylate salts: the first method constitutes anion exchange of chloride salts with sodium carboxylates, while in the second route, the phosphonium cations were deprotonated with base, followed by the reaction of the resulting phosphine imine with a carboxylic acid. Anion exchange reactions involving sodium/potassium salts of carboxylate ions were carried out in methanol or a methanol/water mixture under reflux (Scheme 1). The reactions of sodium acetate proceeded with all phosphonium chlorides in methanol with precipitation of sodium chloride. The filtrates of each of these reactions were evaporated to obtain crystalline solids, which showed a strong IR absorption around 1590 cm^{-1} characteristic of the carboxylate group and the absorption bands of N−H (around 3100 cm^{-1}) and P−N bonds (between 550 and 1500 cm^{-1}). Crystals suitable for single-crystal X-ray analysis were obtained from the reactions of **1** and **6**. X-ray crystal structure confirmed that **6** underwent complete ion exchange, yielding the salt [P(NHCy)$_4$][CH$_3$COO], while only partial exchange occurred during the reaction of **1**, which gave the mixed anion salt [P(NHPh)$_4$]$_2$[CH$_3$COO][Cl]. Unlike sodium acetate, the reactions of disodium oxalate were sluggish for all phosphonium chlorides due to the poor solubility of reactants, except **4**, which is partially soluble in water. The X-ray structure of the product of this reaction revealed the formation of [P(NH*i*-Bu)$_4$]$_2$[C$_2$O$_4$], **9**. It should be noted that the ^{31}P NMR spectra showed no significant change in chemical shifts upon ion exchange reactions in solution.

The second route to form carboxylates employs the neutral phosphine imine (PhNH)$_3$P(NPh), which is obtained via deprotonation of **1** with a solution of KOH in methanol.[17] The ^{31}P NMR spectrum of **10** shows a considerable upfield shift ($\delta = -4.3$) compared with **1**. The infrared spectrum of **10** exhibits a very strong band at 1282 cm^{-1} characteristic of the P=N bond. Single crystals suitable for X-ray structure analysis were obtained from thf, which yielded the solvate **10**·2thf. In contrast to **1**, the chlorides **2**, **3**, **4**, **5**, and **6** were hydrolyzed in the presence of KOH/MeOH generating the corresponding tris(alkylamino)phosphine oxides.

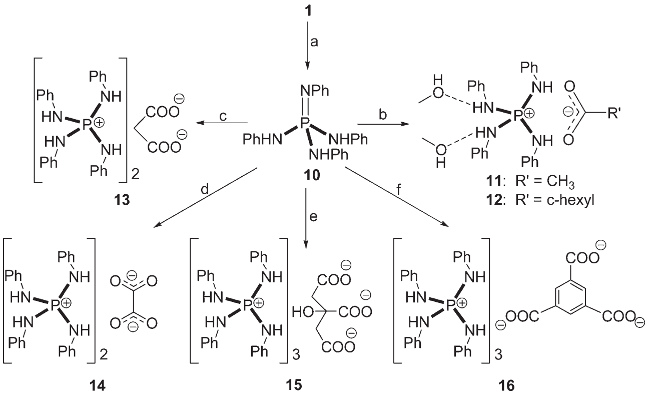
The reprotonation reaction of the phosphorane **10** with monocarboxylic acids, such as acetic acid and cyclohexane carboxylic acid, in 1:1 molar ratio proceeded spontaneously. The ^{31}P NMR spectrum of the reaction mixtures show the phosphonium ion resonance at around 8.0 ppm and the disappearance of the peak due to **10** at δ −4.3 ppm. Extension of this reprotonation strategy to other di- and tricarboxylic acids such as malonic acid, oxalic acid, citric acid, and 1,3,5-benzenetricarboxylic acid resulted in the formation of the corresponding phosphonium salts. The results of all these reactions are summarized in Scheme 2. The crystal structures of **12**, **13**, and **16** were established by X-ray crystallography.

Scheme 1. Preparation of Various Phosphonium Carboxylates 5−9[a]



[a] Reaction conditions: (a) COONa, MeOH, 65 −70 °C, −NaCl; (b) (COONa)$_2$, MeOH/H$_2$O in 1:1 ratio, 65−70 °C, −NaCl.

Scheme 2. Preparation of Various Phosphonium Carboxylates 9−14[a]



[a] Reaction conditions: (a) i. KOH/MeOH, −KCl, ii. H$_2$O; (b) R′COOH, MeOH, 65 −70 °C; (c) CH$_2$(COOH)$_2$, MeOH, 65−70 °C ; (d) (COOH)$_2$, MeOH ratio, 65−70 °C; (e) C(OH)(COOH)(CH$_2$COOH)$_2$, MeOH, 65−70 °C; (f) 1,3,5-C$_6$H$_3$(COOH)$_3$, MeOH, 65−70 °C.

Crystal Structures. The previously reported crystal structure of **1** showed that the phosphonium cations and the chloride anions engage in hydrogen-bonding interactions, forming a zigzag one-dimensional chain structure. The cations are disk-shaped and their four phenyl groups form a near planar arrangement. As a result there are two pairs of NH groups facing in opposite directions. The two NH bonds of each pair are aligned in parallel, acting as a double H-bond donor toward a chloride ion, which in return binds two phosphonium cations. Compound **2**, which contains the least bulky phosphonium cations used in this study, crystallizes in space group *C*2/*c* (Figure 1). It is the only halide structure of this series that does not form a chain but forms a layer structure with the topology of a (4,4) net. Every phosphonium ion binds to four chloride ions via NH···Cl bonds and in return every chloride ion coordinates to four cations. The 2D sheet features a series of 12-membered rings, graph set notation[18] $R^2_4(12)$, each containing two phosphonium and two chloride ions. The corresponding bromide salt **17** exhibits an equivalent layered 2D grid structure in which every ion is connected by hydrogen bonding to four counterions.

The crystal structures of **3**−**5** (Figure 2) exhibit the chain-type topology observed in **1** where each link between phosphonium and chloride ions features two H-bonds to give $R^1_2(6)$ ring

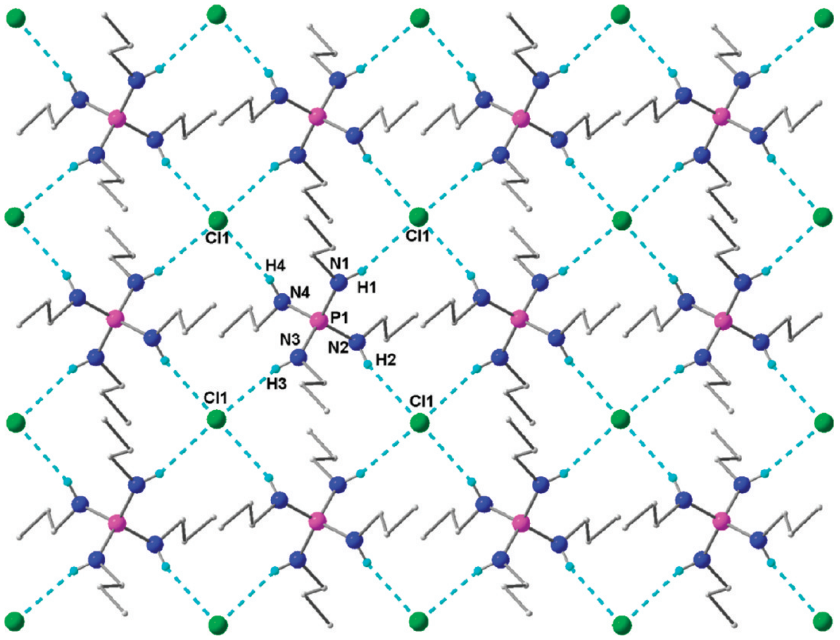


Figure 1. Crystal structure of **2**.

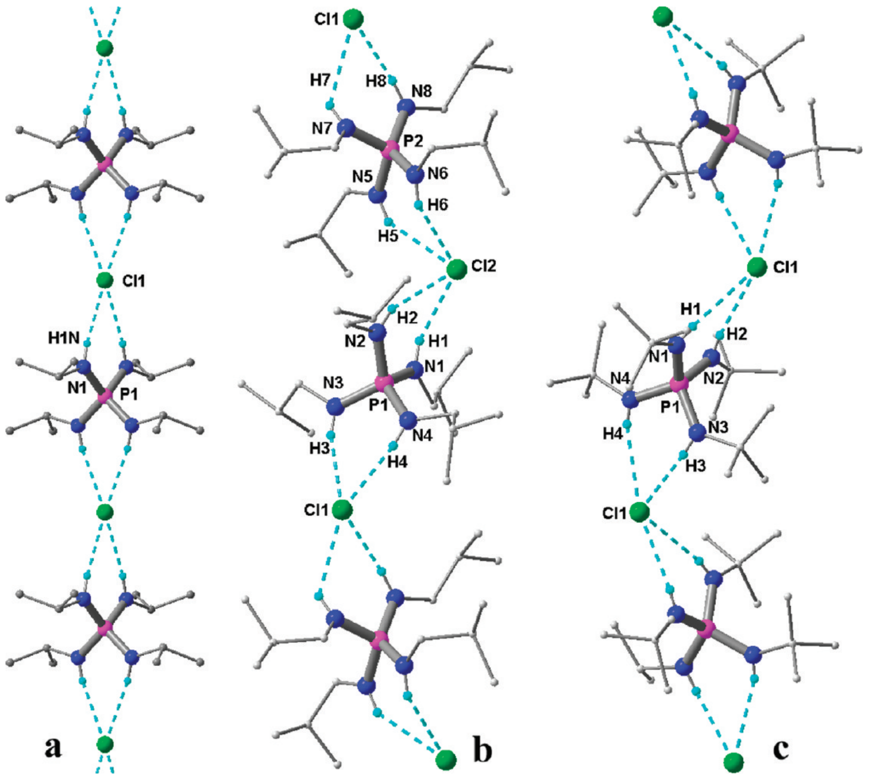


Figure 2. One-dimensional chain structures of **3** (a), **4** (b), and **5** (c).

motifs. The isopropyl derivative **3** crystallizes in the tetragonal space group $P\bar{4}2_1c$. The cation exhibits point group symmetry S_4. The hydrogen-bonded assembly of phosphonium and chloride ions forms a linear chain along [001]. The supramolecular structures of the iso-butyl derivative **4** and the *tert*-butyl derivative **5**, which crystallize in space groups $P2_1/c$ and $P2_12_12_1$, respectively, consist of 1D zigzag chains.

Crystals of the cyclohexyl derivative **6** (Figure 3) were obtained in the form of the hydrate $\mathbf{6}\cdot 2H_2O$, which crystallizes in space group $C222_1$. Again, the ionic moieties form a hydrogen-bonded chain, which however is curled into a helical structure, containing six units of $[P(NHCy)_4]Cl$ per turn. Every turn contains four chloride and four phosphonium ions that reside on general positions and two chloride ions and two phosphonium ions occupying 2-fold rotation axes. The phosphonium ions that are located on general positions show a coordination behavior equivalent to that observed in **1** and **3**−**5** involving all NH groups, while the phosphonium ions located on the 2-fold axes engage with only two NH groups in the bridging of chloride ions.

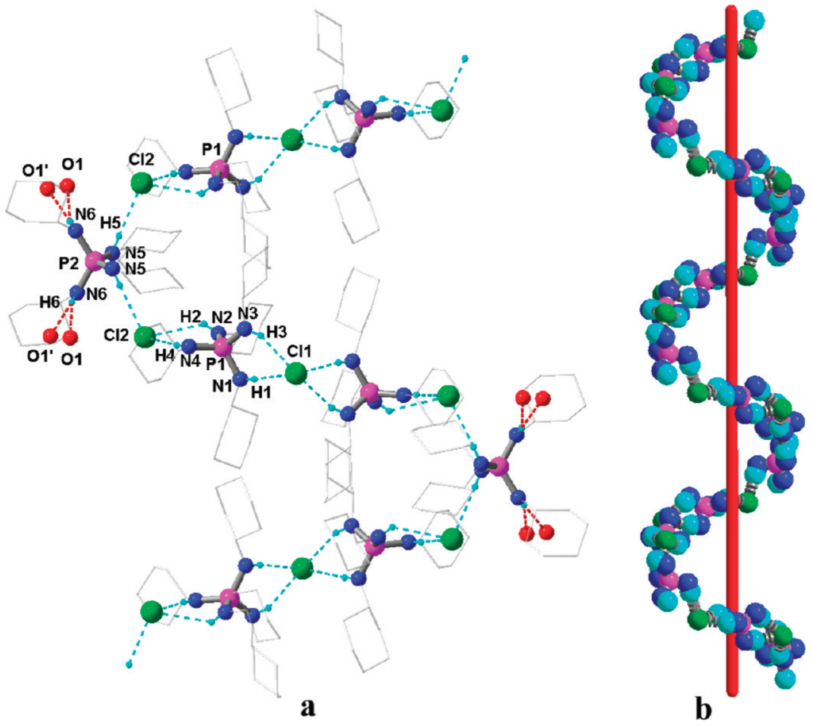


Figure 3. (a) One-dimensional helical chain structure in **6**·$2H_2O$ and (b) view along the helical axis.

The other two NH groups bind to water molecules, which in turn bind to chloride ions, thereby connecting two adjacent helices via H-bonding.

The hydrogen bond distances and angles found in the phosphonium chlorides **1**−**6** are comparable to those of organoammonium chloride salts.[19] The metric parameters associated with the hydrogen-bonding interactions in **2**−**6** are given in Table S3, Supporting Information. The P−N bond distances found in **2**−**6** are similar to **1** and $[P(NH_2)_4]Cl$.[20] Comparison of N−P−N bond angles in **2**−**6** has led to some interesting observations. While the phosphonium bond angles in **2** are close to 109°, two varied types of N−P−N bond angles are found for **3**−**6** indicating different types of deviations from the ideal tetrahedral angle. More acute angles (avg 100.8(9)°) are observed for N−P−N units involved in chelating hydrogen-bonding interactions and wider angles (avg 116.46(7)°) are found for the other N−P−N segments present in nonchelating environment (Table S1, Supporting Information). Although the exact reason for distortion from the perfect tetrahedral geometry in terms of steric and electronic factors is unclear, it appears to be partially controlled by hydrogen-bonding interactions as well.

The crystals of **10**·2thf were obtained by slow evaporation of a thf solution of **10** at room temperature (Figure 4). The molecule **10**·2thf crystallized in the orthorhombic space group *Aba*2. The phosphonium ion occupies a 2-fold axis featuring two pairs of crystallographically unique N-atoms. The P1−N2 bond distance (1.617(2) Å) is considerably shorter than the P1−N1 distance (1.659(2) Å). This distance is somewhat between P−N bond lengths observed in imino and amino phosphorus compounds. This suggests that the imino group is disordered over the two positions N2 and N2a. Equally the two thf molecules, which are bonded to either side of the phosphonium ion via NH···O contacts, are disordered over two positions. Resolving the disorder gives one thf molecule that is bonded to two amino functions, while the other forms a single contact (Figure 4).

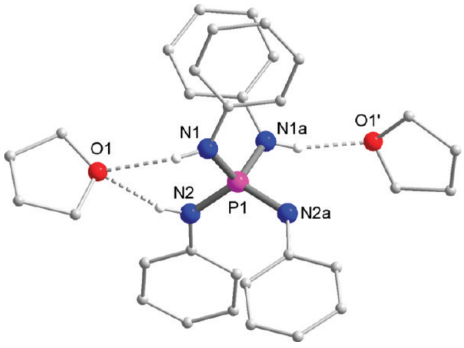


Figure 4. Molecular structure of **10**. The disordered thf fragments are omitted for clarity. P1−N1 = 1.659(2) Å; P1−N2 = 1.617(2) Å; N2−P1−N(1) = 99.93(12)°; N2−P1−N2a = 118.43(18)°; N2−P1−N1a = 115.00(11)°; N1a−P1−N1 = 108.91(17)°. *D*(N1−H1···O1) = 2.20(5) Å; ∠(N1−H1···O1) = 146.9(3)°; *D*(N1−H1···O1) = 2.08(5) Å; ∠(N1−H1···O1) = 162.9(3)°; *D*(N1−H1···O1) = 1.98(5) Å; ∠(N1−H1···O1) = 160.4(3)°.

Structural determination of the phosphonium monocarboxylate salts **7**, **8**, and **12** showed interesting supramolecular variations. The structure of **7** containing mixed chloride and acetate ions is given in Figure 5. It shows the presence of two crystallographically unique phosphonium units (centered on P1 and P2), which are linked together by an alternating array of N−H···O and N−H···Cl hydrogen bonds in a zigzag manner. The chloride ion bonds with the N−H protons in a bridging tetradentate coordination equivalent to that found in **1**. The acetate ion interacts with its neighboring phosphonium segments via both bridging pyramidal and chelating bidentate modes giving rise to the 1D chain propagation.

The X-ray structure analysis revealed that **8** crystallized in the tetragonal space group ($P4_32_12$) in which 'P1' and the acetate carbon atoms sit on the 2-fold axes of rotation

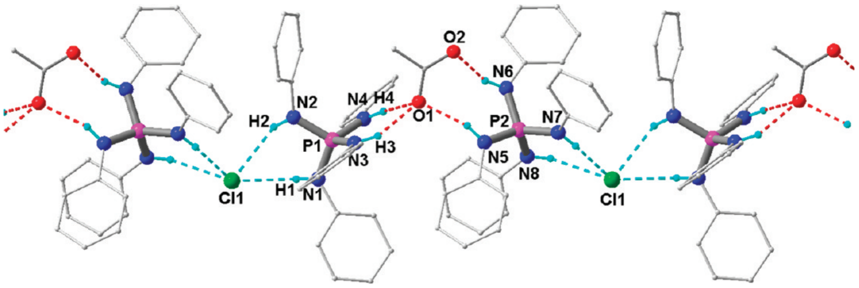


Figure 5. Formation of zigzag H-bond assisted chain in **7**.

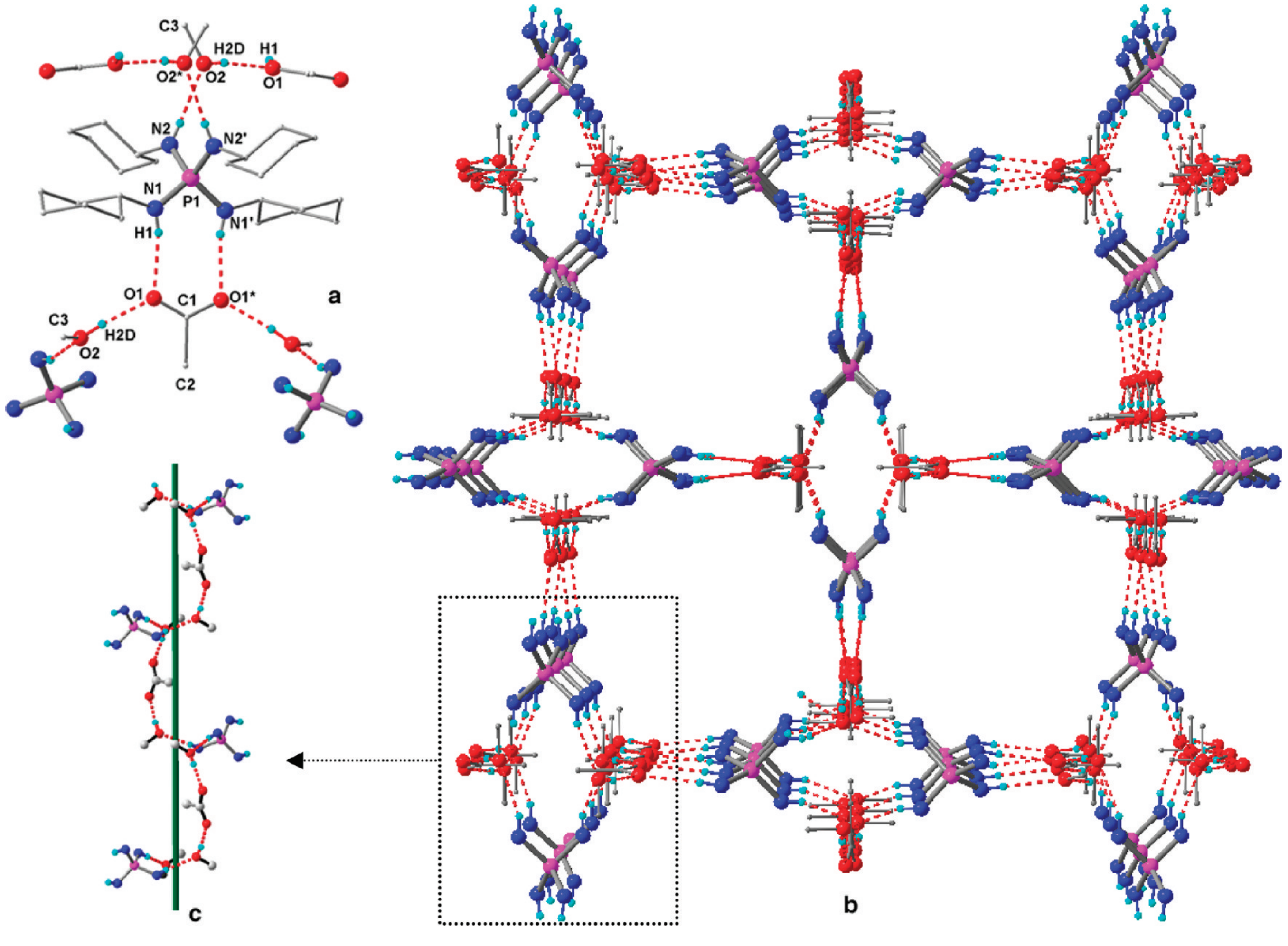


Figure 6. (a) Molecular structure of **8**, (b) formation of 3D grid structure via by N−H···O and O−H···O interactions, (c) view of the helical chains within the grid structure.

(Figure 6a). Compound **12** crystallized in monoclinic space group ($P2_1/c$) where the phosphonium and CyCO$\bar{O}$ units take up the general positions (Figure 7a). The crystal structures of **8** and **12** show that one of their two phosphonium HN−P−NH segments interact with the carboxylate moiety ($CH_3CO\bar{O}$/CyCO$\bar{O}$) through the chelating double hydrogen-bond interaction (Figure 6a). The other segment engages in H-bonding with two methanol molecules, which in turn act as a hydrogen-bond donor to carboxylate ions of the neighboring phosphonium units. Unlike **7**, each carboxylate oxygen is involved in a bifurcated interaction with N−H and O−H protons resulting in the formation of a grid-like three-dimensional network in **8** (Figure 6b) and 2D sheet structure in **12** (Figure 7b). Although the basic structures of **8** and **12** are very similar, their supramolecular structures are apparently different. The change in supramolecular structure is presumably due to the mode of interaction of solvent molecules with the ionic moieties. A closer look at the grid structure in **8** shows the formation of helical chains mediated by solvated methanols, which tether the phosphonium acetate ion pair segments on either side of the helix (Figure 6c). On the other hand, the interaction of methanol, CyCO$\bar{O}$, and two amino protons in **12** forms a zigzag hydrogen-bonded chain (Figure 7b). Thus the helical arrangement in **8** leads to a 3D grid structure and the zigzag arrangement in **12** leads to 2D sheet structure. The N−H···O hydrogen bond distances found in **8** and **12** are stronger, measuring around 1.95(3) Å (avg) and their H-bond angles are close to

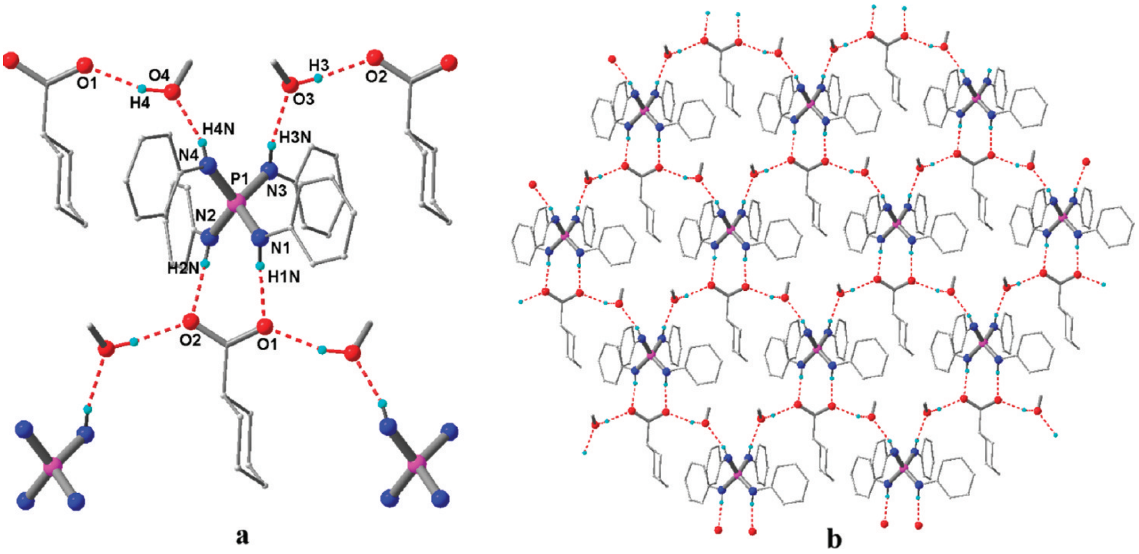


Figure 7. (a) Crystal structure of **12** and (b) its propagation into 2D sheet structure.

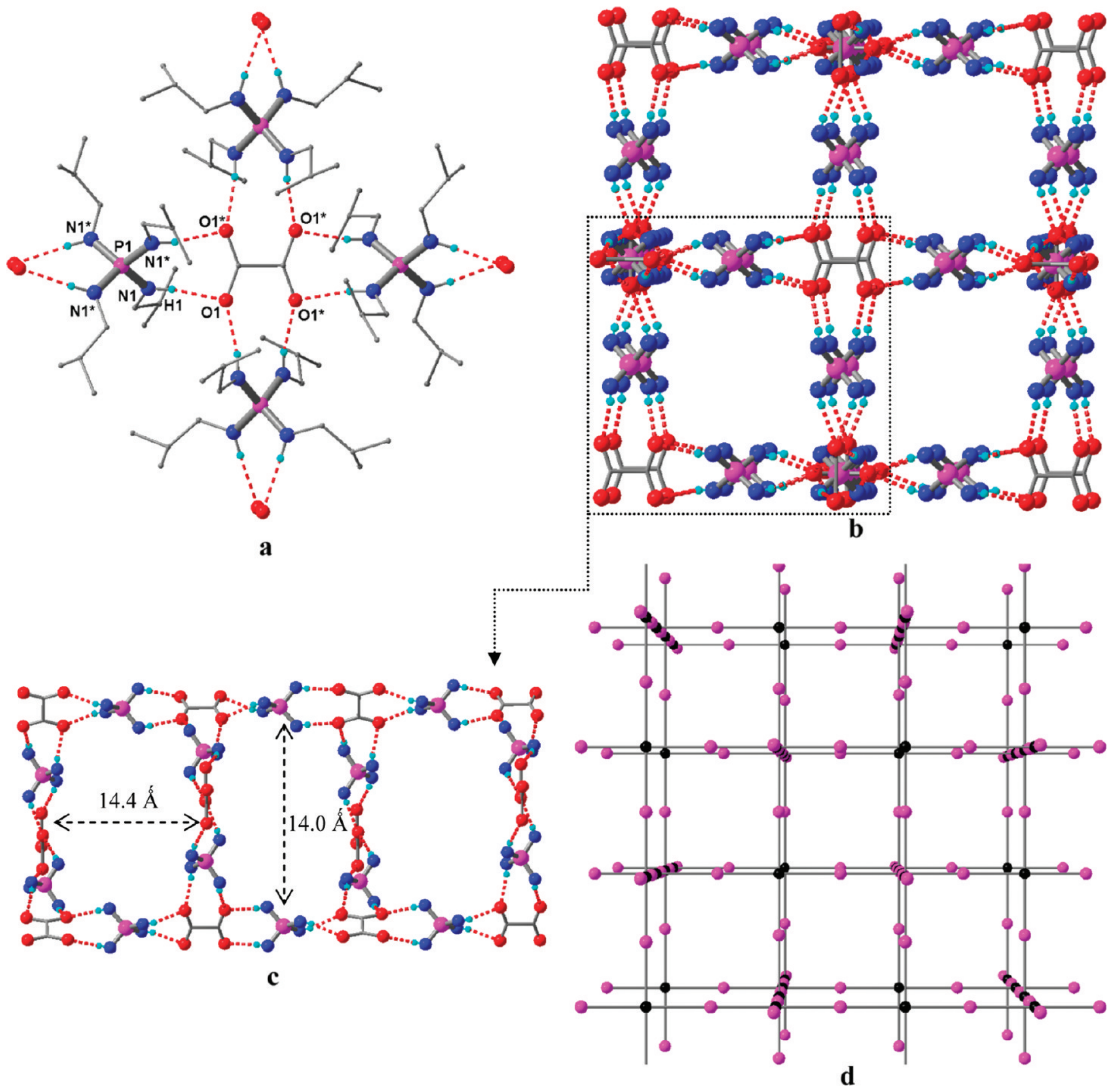


Figure 8. (a) Crystal structure of **9**, (b) formation of cubic 3D network mediated by N−H···O interactions (the isobutyl groups have been omitted for clarity), (c) view of the 28-membered macrocyclic rings, and (d) schematic representation of the arrangement of the cations (pink spheres) and anions (black spheres) in the cubic network.

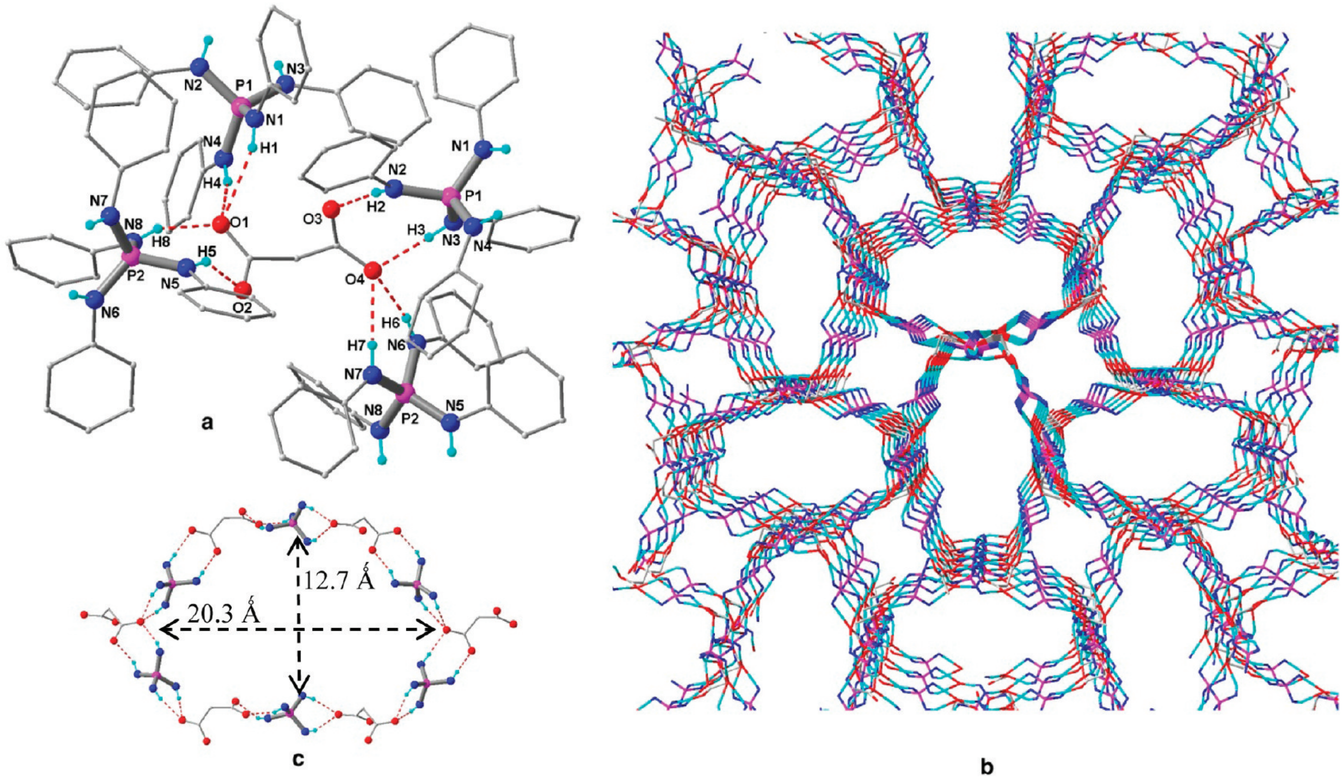


Figure 9. (a) Molecular structure of **13** and its H-bonded neighbors, (b) view of tubular 3D structure (the phenyl rings omitted for clarity), and (c) 52-membered macrocycle within the tubular assembly.

linearity (avg 170.1(3)°). The corresponding methanol donor $R{-}OH\cdots\bar{O}$ distances in these salts are found to be shorter (avg 1.83(3) Å) than the acceptor $NH\cdots OH$ (avg 2.06(2) Å) distances, which showed the stronger affinity of these anions toward H-bonding. The formation of supramolecular structures in **8** and **12** also gives rise to large macrocyclic rings. The 44-membered macrocyclic rings (Figure S5, Supporting Information) in **8** contains five phosphonium units, five acetate ions, and six methanol molecules (graph set $R^{12}_{16}44$). The 28-membered rings in **12** consist of three phosphonium cations, three CyCO$\bar{O}$ ions, and four methanol molecules, which adopt to the graph set $R^{8}_{8}28$ topology.

.The structure of a phosphonium dicarboxylate salt containing the oxalate anion **9** is given in Figure 8. The compound crystallized in the cubic space group $Pn3\bar{n}$ with its asymmetric unit containing one-fourth of the phosphonium moiety and one-fourth oxalate ion. The unique oxalate carbon atom is positionally disordered over four sites, pointing to either a vertical or horizontal alignment of the oxalate ions with respect to the phosphonium cation. Analysis of the hydrogen bonding interactions in **9** shows the formation of a tightly knitted cubic 3D network (Figure 8). Each oxalate ion is surrounded by four phosphonium units in a planar fashion, which offers four pairs of double H-donors (Figure 8a). The oxalate ion in return binds to the four phosphonium units via bifurcated and chelating interactions. On the other hand, the phosphonium HN—P—NH segment on either side of the P-atom is interacting with two oxalate moieties, which are aligned orthogonally to each other (Figure 8a). Thus the orthogonal arrangement of oxalate ions at alternate positions and their bifurcated H-bonding interactions with phosphonium cations help the structure propagate in the 3D network (Figure 8b). The schematic representation of the arrangement of phosphonium (pink spheres) and oxalate ions (black spheres) in the cubic network is shown in Figure 8d, which represents a hitherto unknown type of arrangement of atoms involving amino protons and carboxylate oxygens.[21,22] Each cubic subset of the 3D network is connected at alternate corners and forms large macrocyclic rings of approximately 14 Å diameters (Figure 8c). These rings are formed by six phosphonium and six oxalate ions as represented by graph set $R^{6}_{12}(28)$ topology in their shortest route.

Moving from the rigid oxalate ion to the flexible dicarboxylate ion such as the malonate anion gives rise to a completely different supramolecular structure. The malonate salt **13** crystallizes in the tetragonal space group $I4_1cd$ in which the malonate groups and two phosphonium moieties occupy the general positions. The malonate ion interacts with four phosphonium moieties in which each of its carboxylate ends engages in tetradentate interactions with two phosphonium units through chelating and bridging hydrogen bonds analogous to the acetate ion interaction found in **7** (Figure 9a). Unlike the oxalate ion, which interacts with four phosphonium units in a planar fashion, the malonate ion in **13** hydrogen bonds to four phosphonium units in a concerted manner. The overall result of these hydrogen-bonding interactions in **13** is the generation of a tubular three-dimensional network (Figure 9b). The tubular structure can be viewed as the stacking of an array of large macrocyclic rings facilitated by the flexible nature of malonate chains (Figure 9c). These rings are nanoscopic in dimension and are fused by the aid of six phosphonium and six malonate moieties (graph set $R^{10}_{12}(52)$).

The phosphonium salt **16** containing the 1,3,5-benzene tricarboxylate trianion (trimesic anion) crystallized in the monoclinic space group Pc. The asymmetric unit of this molecule consists of six phosphonium moieties and two

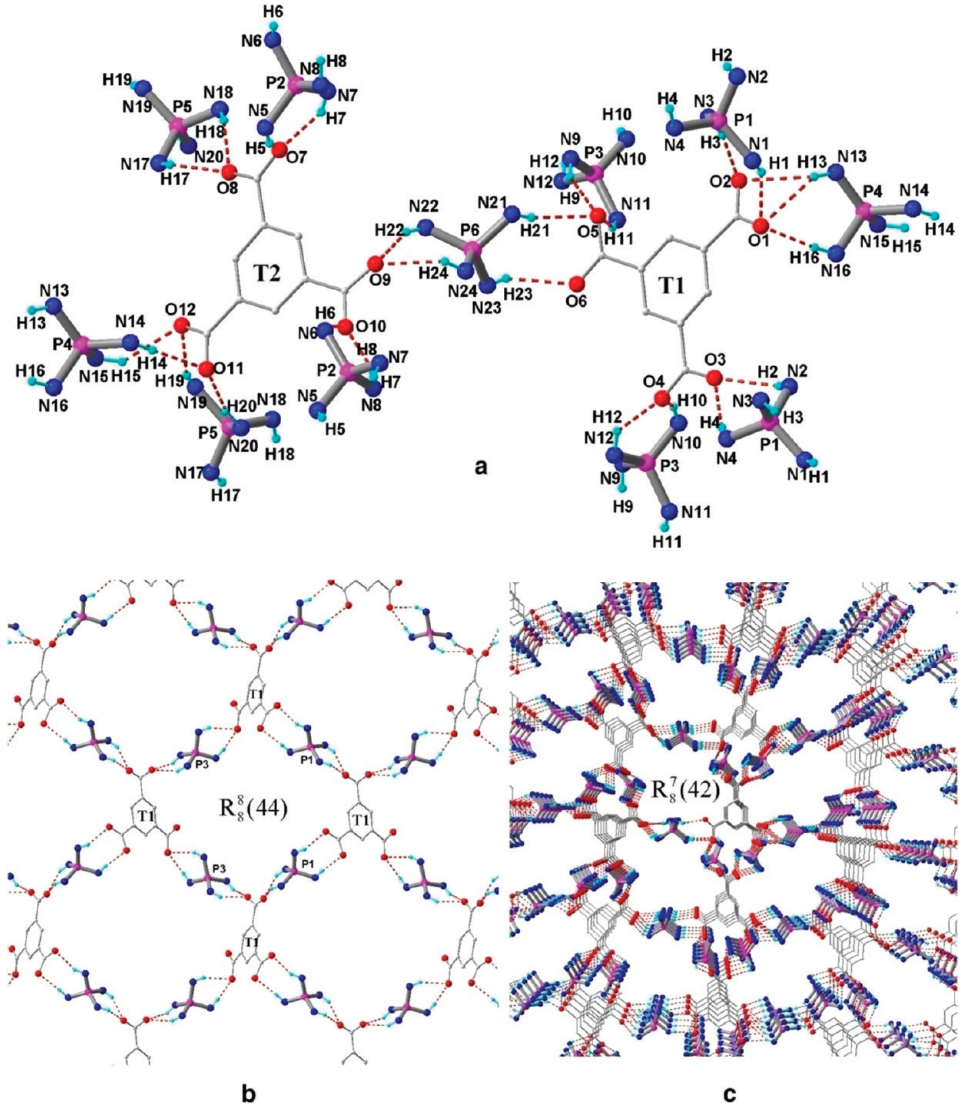


Figure 10. (a) Molecular structure of **16** with its immediate H-bonded neighbors (the phenyl rings on amino groups have been omitted for clarity), (b) view of the individual planar (4,4) sheet within the 3D assembly and (c) formation of the 3D supramolecular network mediated by N−H···O interactions.

trianions, which are labeled for convenience as T1 and T2 (Figure 10a). Each trianionic motif is surrounded by six phosphonium cations with every carboxylate end hydrogen bonded to two phosphonium units via tetradentate interactions. The stepwise assembly of the 3D supramolecular structure can be understood as follows. Out of the six phosphonium moieties, two of them, centered on P1 and P3, are solely involved in hydrogen bonding the trimesic unit labeled T1 into a planar (4,4) sheet (Figure 10b). Likewise, the phosphonium units P2 and P5 tether the trimesic units of T2 in the 2D manner. The sheets of T1 and T2 superimpose onto each other and are further linked by the remaining two phosphonium moieties, centered on P4 and P6, leading to a 3D network. Formation of the three-dimensional structure in **16** accompanies two different types of macrocyclic rings. While the individual (4,4) sheets of T1 and T2 form $R_8^8(44)$ rings, macrocycles situated between the sheets of T1 and T2, involving the bridging phosphonium connectors of P4 and P6, form $R_8^7(42)$ rings.

The hydrogen bond details associated with the compounds **7**−**16** are listed in Table S4, Supporting Information. The N−H···O bond distances and angles found in them are comparable to the carboxylate salts of protonated amines.[23] In all these carboxylate salts, the phosphonium moieties interact with the carboxylate groups in a chelating double H-interaction. As a result N−P−N bond angles in these salts deviate from the ideal tetrahedral angle in which more acute angles of around 100° are again found for the N−P−N segments involved in chelating interactions (Table S3, Supporting Information). A thermogravimetric analysis (TGA) was conducted on the samples of some of the representative phosphonium carboxylates (Supporting Information). The thermal behavior of all measured samples indicates that their supramolecular structures are stable at relatively high temperatures and range between 150 and 300 °C. This information can thus be corroborated with strong hydrogen-bonding interactions found for the phosphonium carboxylate salts.

In summary, we have comprehensively studied the supramolecular behavior of organoamino-substituted phosphonium cations in presence of halide or carboxylate anions or both. The dimensionality of supramolecular structure exhibited by the phosphonium halides can be varied depending on the steric bulk on the amino substituent. Thus, interesting examples of 2D sheet structures and 1D structures containing linear, zigzag, and helical chains are obtained. The phosphonium cations containing carboxylate anions are prepared by two routes: by anion exchange reactions with phosphonium chlorides and by protonation of neutral phosphine(amine)-imine, P(NPh)(NHPh)$_3$. While the phosphonium cations containing monocarboxylate anions show solvent-assisted supramolecular structures, the corresponding phosphonium di- and tricarboxylate salts display intricate charge-assisted hydrogen-bonding interactions forming tightly knit 3D structures. All these compounds were characterized by IR, NMR, and X-ray crystallographic techniques. Thermogravimetric studies performed on the phosphonium carboxylates show good thermal stabilities for their supramolecular assemblies. Currently, work is in progress toward utilizing these phosphonium scaffolds as multimodal ligands for obtaining polynuclear clusters, coordination cages, and porous coordination polymers. Possible synthesis of such porous coordination polymers based on phosphonium building blocks may pave way for the quantitative entrapment of gaseous molecules.[24]

Experimental Section

General Remarks. All manipulations involving phosphorus pentachloride were performed under dry nitrogen atmosphere in standard Schlenk glassware. Solvents were dried over potassium (thf, hexane) and sodium (toluene). The precursor compounds, phosphonium chlorides **1**−**6** and phosphonium bromide **17** were prepared as described previously.[15] PCl$_5$ and primary amines were purchased from Aldrich and used as received. The carboxylate precursors were locally procured (SPECTROCHEM, India) and used as received. NMR spectra were recorded on a 400 MHz Varian FT spectrometer (^{1}H NMR 400.13 MHz, ^{13}C{^{1}H} NMR 100.62 MHz, ^{31}P{^{1}H} NMR 161.97 MHz) at room temperature using SiMe$_4$ (^{1}H, ^{13}C) and 85% H$_3$PO$_4$ (^{31}P) as external standards. FT-IR spectra were taken on a Perkin-Elmer spectrophotometer with samples prepared as KBr pellets. Melting points were obtained using an Electrothermal melting point apparatus and are uncorrected. Detailed experimental procedures for the compounds **7**−**16** and **19** are described in the Supporting Information.

Crystallography. Reflections were collected either on a Bruker Smart Apex II CCD diffractometer at 293 K or on a Bruker Smart Apex CCD diffractometer at 100 K using Mo Kα radiation (λ = 0.71073 Å). Structures were refined by full-matrix least-squares against F^2 using all data (SHELX).[25] Non-hydrogen atoms were refined aniostropically. Hydrogen atoms were constrained in geometric positions to their parent atoms, with the exception of N-bound H-atoms, which were refined without constraints. Crystallographic data of **2**, **3**, **4**, **5**, **6**·2H$_2$O, **7**, **8**, **9**, **10**·2thf, **12**, **13**, **16**, and **17** are listed in Table S1, Supporting Information. The crystal structure of **4** contains one disordered isobutyl group and one disordered isobutyl amino group. The solvated molecules of water and thf in the crystal structures of **6**·2H$_2$O and **10**·2thf, respectively, are disordered. One phenyl ring in **7** and three phenyl rings in **13** are disordered. Atom positions of the disordered groups in **4**, **6**·2H$_2$O, **10**·2thf, and **13** were split over two positions and refined isotropically using similar-distance restraints. The disordered phenyl group of **7** was split over three positions and isotropically refined. Crystals of **4** and **13** diffracted weakly lacking observed reflections at higher angles; thus a cutoff at 2θ = 45° was applied. Although the unit cell parameters of **16** show a good fit for orthorhombic P, both the diffraction pattern and the crystal structure shows monoclinic P symmetry and no sign of twinning.

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Supporting Information Available: Synthetic procedures for **7**−**17**, crystallographic data in table format as well as in CIF format, table of bond lengths and bond angles for **1**−**17**, crystal structure of figures for **17**, additional figures for **6**·2H$_2$O, **8**, **12**, and **16** and TGA data. This material is available free of charge via the Internet at http://pubs.acs.org.

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