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Topological Classification and Supramolecular Chirality of 2_1-Helical Ladder-Type Hydrogen-Bond Networks Composed of Primary Ammonium Carboxylates: Bundle Control in 2_1-Helical Assemblies

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Abstract: The supramolecular chirality of 1D ladder-type hydrogen-bond networks composed of primary ammonium carboxylates was determined based on topological considerations. Chirality in such networks is based on the absolute configuration of the primary ammonium cation, which arises from discrimination between the two oxygen atoms of the carboxylate anion. The configurations of the cations and anions generate topological diversity in the networks, which are classified into six subgroups. In the Cambridge Structural Database, salts based on ladder type **1** constitute over 70 % of salts with a 1D-ladder-type network. Ladder type **1**, based on a 2_1-axis, is not superimposable on its mirror image, which leads to the first definition of right- or left-handedness of 2_1-helicity on the basis of supramolecular tilt chirality. Helical assemblies of 2_1-type with triaxial chirality can be assembled in various ways to yield chiral bundles and crystals. On the basis of these considerations, we constructed clay mimic structures with several bundle patterns by connecting the hydrogen-bond networks by using bifunctional molecules. These results open up the possibility of in-depth crystal engineering based on hydrogen-bond topology.

Keywords: ammonium carboxylates · chirality · hydrogen bonds · supramolecular chemistry · topology

Introduction

The topological study of networks has transcended the frameworks of research fields and been applied to a wide range of scientific research areas, which includes the Internet,[1] DNA,[2] polymer,[3] and other topologies.[4] Recently, the study of topology has also contributed to the development of supramolecular architectures based on coordinate or covalent bonds, such as coordination polymers,[5] catenanes, and knots.[6]

Interestingly, hydrogen-bond networks themselves have been shown to exhibit topological diversity, mainly through simulation studies of small molecules, such as water or methanol.[7] However, these experimental investigations have been limited to the vapor phase[8] or the crystalline state.[9]

Over the past two decades, the field of crystallographic study has undergone considerable development owing to outstanding contributions, such as graph sets and supramolecular synthons.[10] Many organic salts serve as representative synthons owing to their advantageous features, such as 1) strong charge-assisted hydrogen bonding through proton transfer, for example, from acids to amines; 2) clear directionality; and 3) a wide variety of possible cation–anion combinations.

While investigating synthon-directed crystal engineering using these salts, we noticed a topological aspect to the hydrogen-bond networks of primary ammonium carboxylates (Figure 1). The cations and anions act as tridentate hydrogen-bond donors and acceptors, respectively. This confers a notable feature on the carboxylate anion: one of the two oxygen atoms of the carboxylate anion (O(α)) acts as a two-hydrogen-bond acceptor, whereas the other (O(β)) acts as a one-hydrogen-bond acceptor (Figure 1a, inside the solid box). This feature generates topological diversity and leads

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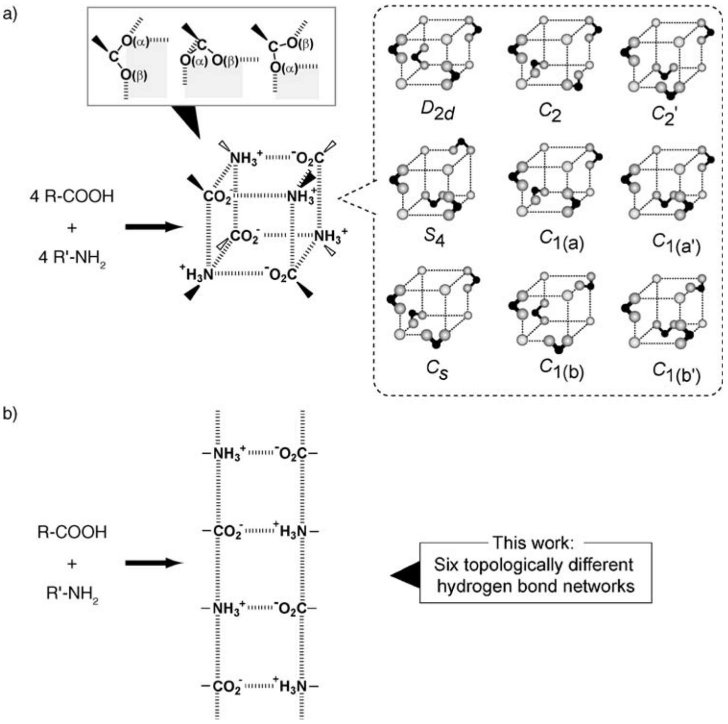


Figure 1. a) Pattern diagrams of a pseudo-cubic hydrogen-bond network, nine possible topologies for the pseudo-cubic network (box with dashed line), and three possible alignments of carboxylate anions (box with solid line). b) Pattern diagrams of ladder hydrogen-bond networks composed of primary ammonium carboxylates.

to a novel interpretation of supramolecular assemblies and chirality that cannot be represented by the commonly used graph set.

In our previous study we demonstrated the topological diversity of pseudo-cubic hydrogen-bond networks composed of primary ammonium triphenylacetates.[9c] Nine different topologies that combine three different alignments of four carboxylate groups at the vertices of the cube (Figure 1a) were ascertained. Such topological features may be observed in one-dimensional ladder hydrogen-bond networks (Figure 1b). Herein we report a topological interpretation of ladder networks composed of primary ammonium carboxylates, which enables us to give a reasonable definition of supramolecular chirality in ladders and bundles. Moreover, this idea opens up the possibility of in-depth crystal engineering based on hydrogen-bond topology in bundles composed of 2_1-helical assemblies of bis(primary ammonium) dicarboxylates.

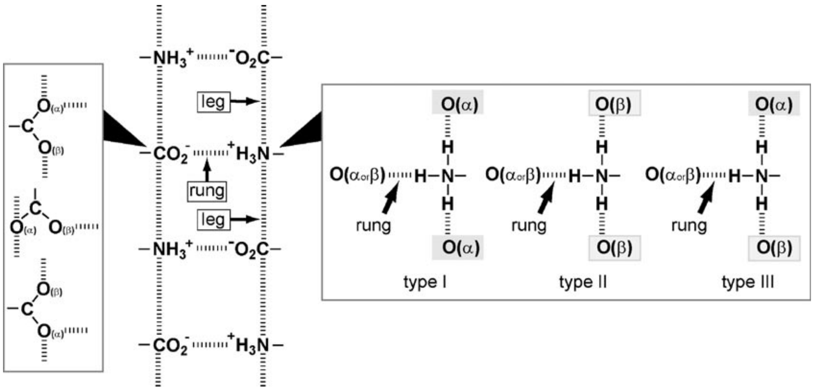


Figure 2. Hydrogen-bonding types of primary ammonium cations and carboxylate anions used in the ladder networks.

Results and Discussion

Topology of ladder networks: Based on this topological insight, we investigated ladder hydrogen-bond networks from the viewpoint of the configurations not only of the carboxylate anions, but also of the primary ammonium cations (Figure 2). Similar to their configurations in the pseudo-cubic network described above, the carboxylate anions can be aligned in three different ways on the ladder (Figure 2, left). Therefore, the ammonium cations show three different hydrogen-bonding types, based on the bonding modes of the two carboxylate anions to which they are connected in the direction of the leg of the ladder: two O(α)-type anions (type I), two O(β)-type anions (type II), or one O(α) and one O(β) anion (type III; Figure 2, right).

As shown in Figure 3, each nitrogen atom forms four covalent bonds with one ladder substituent and three hydrogen atoms, and each hydrogen atom forms a hydrogen bond with either O(α) or O(β). This results in a total of eight ($=2^3$) different ammonium cation types with three subgroups. In the case of types I and II, both hydrogen atoms in the leg direction form hydrogen bonds with the same type of carboxylate anion: O(α) (type I) or O(β) (type II). Therefore, these four ammonium cation types are achiral (Figure 3, left). In contrast, for type III, three types of hydrogen atom are distinguishable; one hydrogen forms part of the rung of the ladder, and the other two (the leg hydrogens) each form one hydrogen bond with O(α) and O(β). This means that nitrogen atoms of type III have four distinguishable bonds in an sp^3-hybrid-orbital state, and are therefore chiral. The chiral nitrogen atoms are classified as N(a) or N(c) according to the alignment of the four bonds.[11]

This enantiomeric discrimination between nitrogen atoms plays a decisive role in the topological classification of the ladder networks. Figure 4 shows a well-known ladder network composed of primary ammonium carboxylates.[12] Although this network has been reported by many groups since 1976,[13] it has not yet been investigated from a topological viewpoint. The network has a 2_1-helical axis, and its helicity can be determined as follows: First, we identify the configuration of the ammonium cations, which confirms that

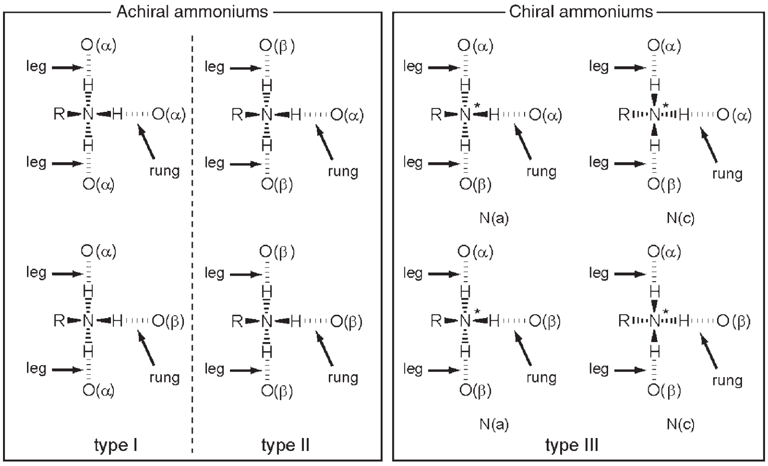


Figure 3. Four achiral and four chiral nitrogen atoms present in the networks.

one network only contains N(a) atoms (Figure 4, left), whereas the other only contains N(c) atoms (Figure 4, right). Second, we determine helicity and handedness in terms of supramolecular tilt chirality.[14] Figure 4 shows a section of the hydrogen-bond network with the sequence ···O···HNH···O···HNH··· (shown in blue and red), which forms helical stairs. When the NH···O bonds of the rung and the steps of the stairs are inclined to the left (Figure 4, left) or right (Figure 4, right) of the front of the 2_1 axis, the helical networks are defined as left- (*M*) or right-handed (*P*), respectively. Third, we confirm that both network and stairs have three distinguishable axes, such as up and down, left and right, and in and out. The up and down direction is based on the carboxylate groups (shown in yellow in Figure 4). Herein, helicity and handedness are schematically displayed as colored helical tapes with arrows.

It is worth clarifing the differences between the ladder and the pseudo-cubic networks. The former is an infinite line of six-membered rings (excluding hydrogen). Figure 5shows schematically that four continuous six-membered rings (Figure 5b) may be rolled together to produce a pseudo-cubic network with S_4 topology (Figure 5a), and the reverse is also true. Thus, opening the nine topologically different types of pseudo-cubic network (Figure 1a) theoretically gives fifteen different combinations of the four continuous rings. The resulting ladder network from the pseudo-cubic network with S_4 topology (Figure 5b), however, differs from those networks previously reported (Figure 5c and d) in terms of the absolute configurations of the nitrogen atoms.

Screening ladder networks: More than 2000 compounds that contain ammonium carboxylate were found in the Cambridge Structural Database (CSD version 5.27). We performed a search for structures that contained at least two molecules composed of one primary amine and one carboxylic acid, excluded any extra acids, bases, or metals, and obtained 317 entries. The pie chart shown in Figure 6 shows

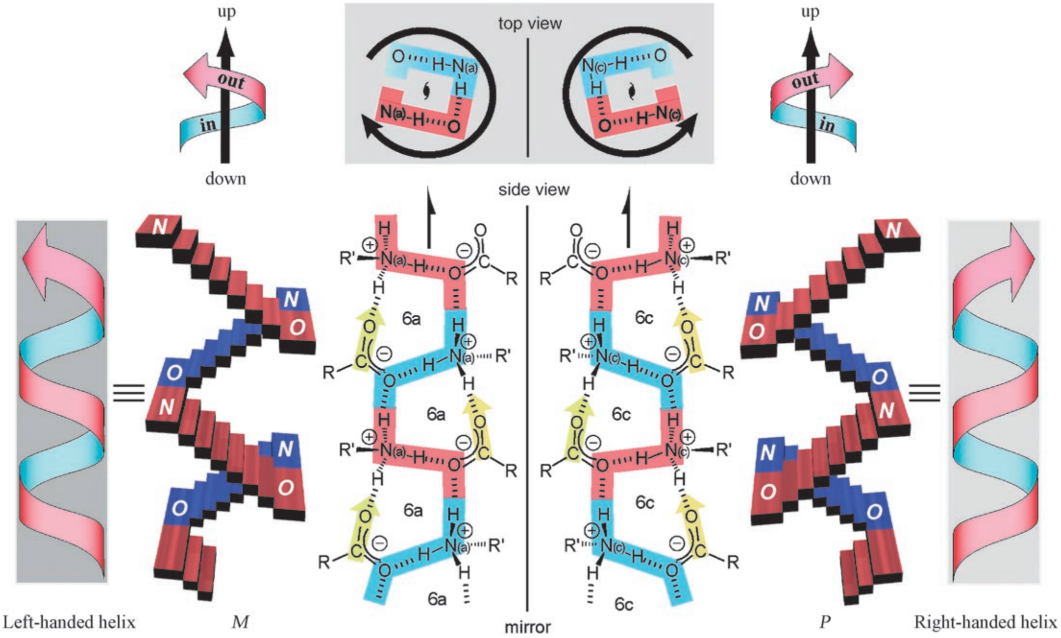


Figure 4. Schematic representation of the chiral 2_1-helical networks to show their left- and right-handedness.

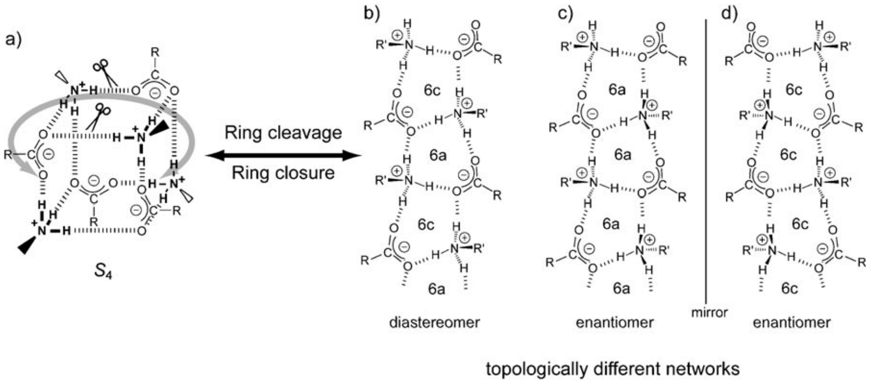


Figure 5. Relationship between pseudo-cubic and ladder networks: a) pseudo-cubic hydrogen-bond network with S_4 topology; b) ladder network obtained from the pseudo-cubic network; c) and d) known ladder-shaped hydrogen-bond networks. The rings are labelled a and c after the type of nitrogen atoms at the bottom of the rings.

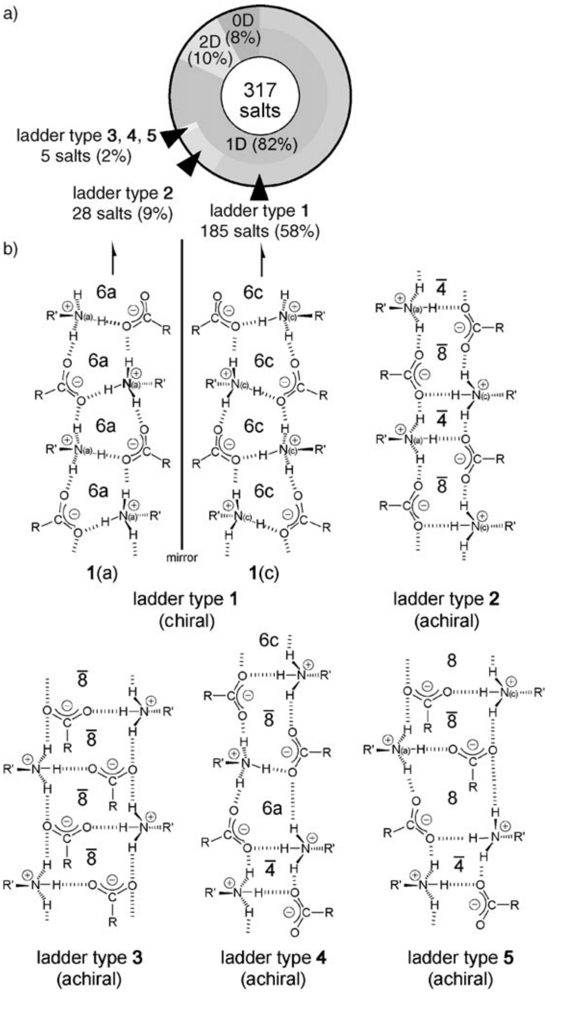


Figure 6. a) Classification of CSD compounds that contain hydrogen-bond networks composed of primary ammonium carboxylates. b) Pattern diagrams of the ladder hydrogen-bond networks composed of primary ammonium carboxylates (denoted as ladder types **1**–**5**).

the distribution of hydrogen-bond networks with charge-assisted NH···O hydrogen bonds, which are classified into three categories according to their dimensionality. The 0D, 1D, and 2D networks constitute 8, 82, and 10% of salts, respectively (see the Supporting Information). The database contains only four salts with pseudo-cubic networks.[15]

We classified the 1D networks into five ladder-shaped types (ladder types **1**–**5** in Figure 6) based on the combination of four-, six-, and eight-membered rings (excluding hydrogen), as defined in our previous work.[9c] The repeating units contain up to four rings. Ladder type **1** dominates and comprises 72% of 1D networks and 58% of all primary ammonium carboxylate entries. Most of the ladder type **1** networks are constructed along a 2_1-helical axis with chiral ammonium cations. The proportion of 58% is in agreement with the proportion of organic crystals with 2_1-helical axes in the CSD.[16] Networks of ladder types **2** and **3** often contain inversion centers (bars over the ring numbers in Figure 6 denote the presence of inversion centers within the rings). The cations of ladder type **2** belong to cation type III, but as N(a) and N(c) are arranged in alternating fashion, ladder type **2** is achiral. In contrast, the cations of ladder type **3** belong to type I, and thus the network is also achiral. Low-symmetry ladder types **4** and **5** contain two independent anions and cations in the asymmetric unit ($Z'=2$). In ladder type **4**, cations of types I and II are aligned with inversion centers, whereas in ladder type **5**, cations of types I and III are aligned with inversion centers.

Assembly of helical networks: These ladder networks may assemble in various ways to afford bundles with supramolecular chirality. We investigated the assembly of ladder type **1** networks with directionality and chirality on the basis of 185 crystal structures from the CSD (see the Supporting Information). As mentioned above, networks of ladder type **1** feature supramolecular chirality with triaxial directionality, which enables us to classify the bundles into seven types that are named after typical space groups (Figure 7): enantiomers of $P2_1$-type (including $C2$ and $P4_1$) and $P2_12_12_1$-type, $P2_1/n$-type (including $P2_1/a$, $P2_1/c$, $C2/c$, $I4$- and Pn), $Pbn2_1$-type (including $Pca2_1$), and $Pnma$-type. Of the 185 salts from the CSD, all salts composed of optically pure chiral compounds belong to $P2_1$-type or $P2_12_12_1$-type. In contrast, many of the achiral and racemic salts assemble in $P2_1/n$-type bundles. Only three crystals show $Pbn2_1$-type assembly. $Pnma$-type crystals with an alternating arrangement of four ladder type **1** networks with opposite chirality and direction were not observed. Interesting examples include one compound that forms chiral crystals from achiral components, which involves thirteen crystals with $P2_1$-type or $P2_12_12_1$-type assembly,[17] and another that consists of two pairs of

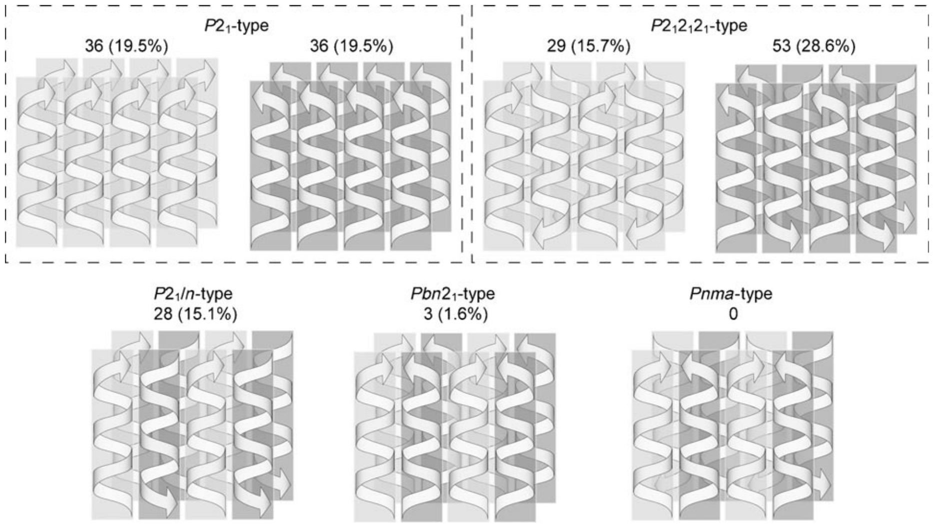


Figure 7. Schematic representation of the seven types of bundle that involve ladder type **1** networks with triaxial directionality, and the number (and proportion) of each type found.

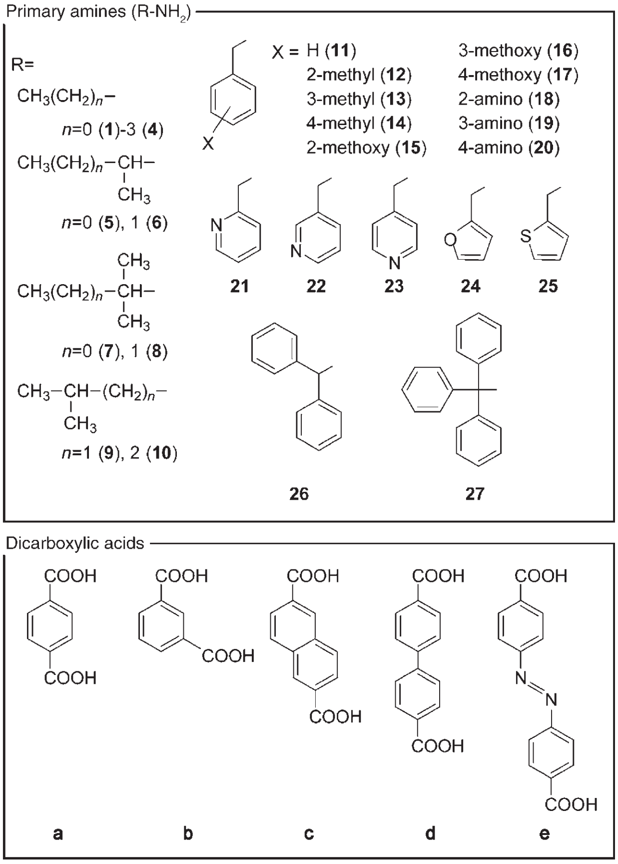
polymorphic crystals composed of chiral salts, one crystal of which, surprisingly, contains $P2_12_12_1$-type bundles with right-handed helices, whereas the other contains left-handed bundles.[18] These examples suggest the possibility of controlling bundles of helical assemblies based on a wide variety of organic salts.

Bundle control in 2_1-helical dicarboxylate-based networks: Next, we describe bundle control in ladder type **1** that contain dicarboxylic acids for the purpose of supramolecular synthon-directed crystal engineering. Many crystal structures composed of bis(primary ammonium) dicarboxylates have been reported by this group and others.[19–21] Matsumoto et al. investigated muconate salts with a variety of hydrogen-bond networks.[20] We have also reported clay mimic structures composed of layers constructed by connecting ladder type **1** with various types of phenylene tecton.[21] The clay mimic structures may be classified according to the direction and helical handedness of ladder type **1** (Figure 8). When the ladders are linked with dicarboxylates, four different structures are possible: chiral-parallel type (CP type), chiral-antiparallel type (CA type), racemic-parallel type (RP type), and racemic-antiparallel type (RA type). In contrast, molecules of ladder type **2** form only one structure owing to the existence of inversion centers in the network.

Herein, we employed five dicarboxylic acids with phenylene tectons as rotatable spacers (Scheme 1). Various salts were prepared by mixing the appropriate primary amines and dicarboxylic acids at a 2:1 molar ratio in methanol. Evaporation of the solutions yielded powdered salts, which were recrystallized from a mixture of methanol and a poor solvent, such as acetonitrile or benzene. The resulting crystals were subjected to X-ray single-crystal analysis.

Terephthalate salts crystallized very easily, whereas isophthalate salts often formed a sticky paste and seldom crystallized. For dicarboxylates with spacers longer than terephthalate, it was difficult to obtain crystals for measurement as a result of their decreased solubility in methanol. X-ray single crystallographic analysis of the salts (see the Supporting Information) revealed that the resulting clay mimic structures could be classified into four categories (Table 1): three with ladder type **1**, and one with ladder type **2**. These crystals were obtained at a molar ratio of 2:1, which corresponds to the ratio of salt formation.[22]

Most of the terephthalate salts formed structures of RA type, in which ladder type **1** of opposing direction and helix configuration are connected through linker molecules. Figure 9c shows a packing diagram of **5a** viewed from the crystallographic b and c axes as a typical example of a clay mimic structure with ladder type **1**. In this structure, ladder type **1** runs along the crystallographic b axis with the 2_1-heli-



Scheme 1. Primary amines (**1**–**27**) and dicarboxylic acids (**a**–**e**) employed in salt formation.

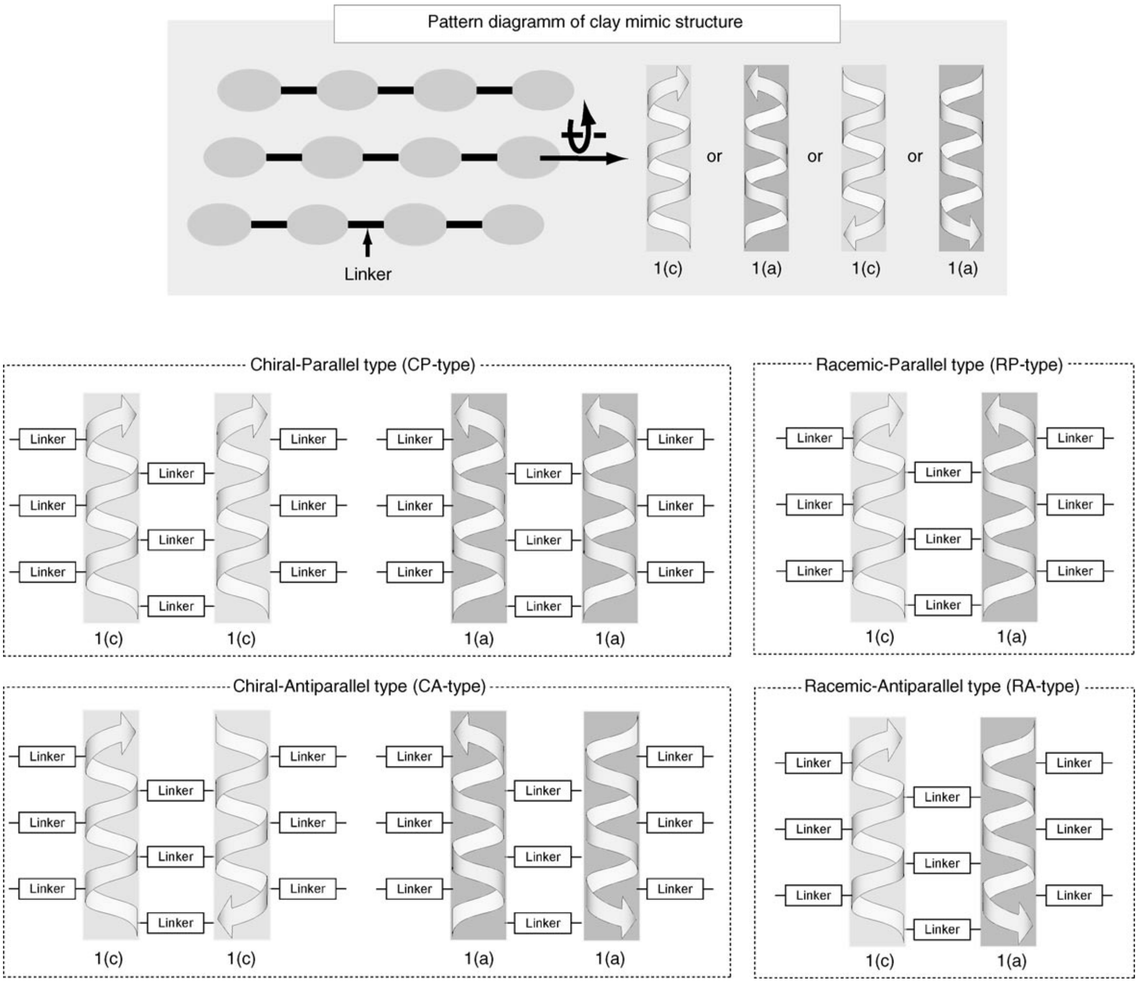


Figure 8. Schematic representation of the four different clay mimic structures constructed by connecting ladder type **1** networks with dicarboxylic acids.

Table 1. Classification of the different types of clay mimics.

Type of clay mimic	Salt	
Ladder type **1**	CP-type	Not obtained
	CA-type	**9a**[a]
	RP-type	**5b**, **8b**[b]
	RA-type	**4a**, **5a**, **8a**,[b] **10a**, **11a**, **14a**, **17a**, **18a**, **20a**, **22a**, **24a**, **25a**, **26a**, **6c**, **14c**, **8d**,[b] **11e**
Ladder type **2**		**16a**, **21a**, **8c**, **17c**

[a] We could not determine the absolute structure of **9a** from the anomalous dispersion. [b] Ref. [21].

ces in an antiparallel arrangement. Figure 9d shows a packing diagram of **16a** viewed from the crystallographic b and c axes as a typical example of a clay mimic structure with ladder type **2**. In this case, the terephthalate anions align in parallel fashion.

In contrast, two isophthalate crystals were found to be of RP type, with the 2_1-helices arranged in parallel fashion (Figure 9b). The alignment of the helices is derived from the *meta*-orientation of the two carboxyl groups, which are aligned at approximately 60° to the supramolecular synthon. The RP-type layer is stacked in an antiparallel fashion, which results in the first example of a *Pnma*-type assembly of 2_1-helices.

Only **9a** contained benzene molecules between the layers. Surprisingly, in contrast with the other salts, compound **9a** crystallized without mirror symmetry in the lattice, which resulted in chiral crystals (Figure 9a). The inclusion of guest molecules in the hydrophobic space may result in deformation of the layer structure, which induces the two ammonium cations to assume different conformations. Incidentally, contortion of this type of structure may lead to the formation of a CA-type structure.

In all of the crystals, the two carboxyl groups of the dicarboxylic acid molecule formed identical hydrogen-bond networks, predominantly ladder networks. Charge-assisted NH···O bonds were formed preferentially, with little formation of weak hydrogen bonds, such as CH···N or CH···S, among the heterocyclic substituents. However, in crystal structures that contained amino-substituted benzylammonium ions (**18a** and **20a**), non-charge-assisted NH···O hydro-

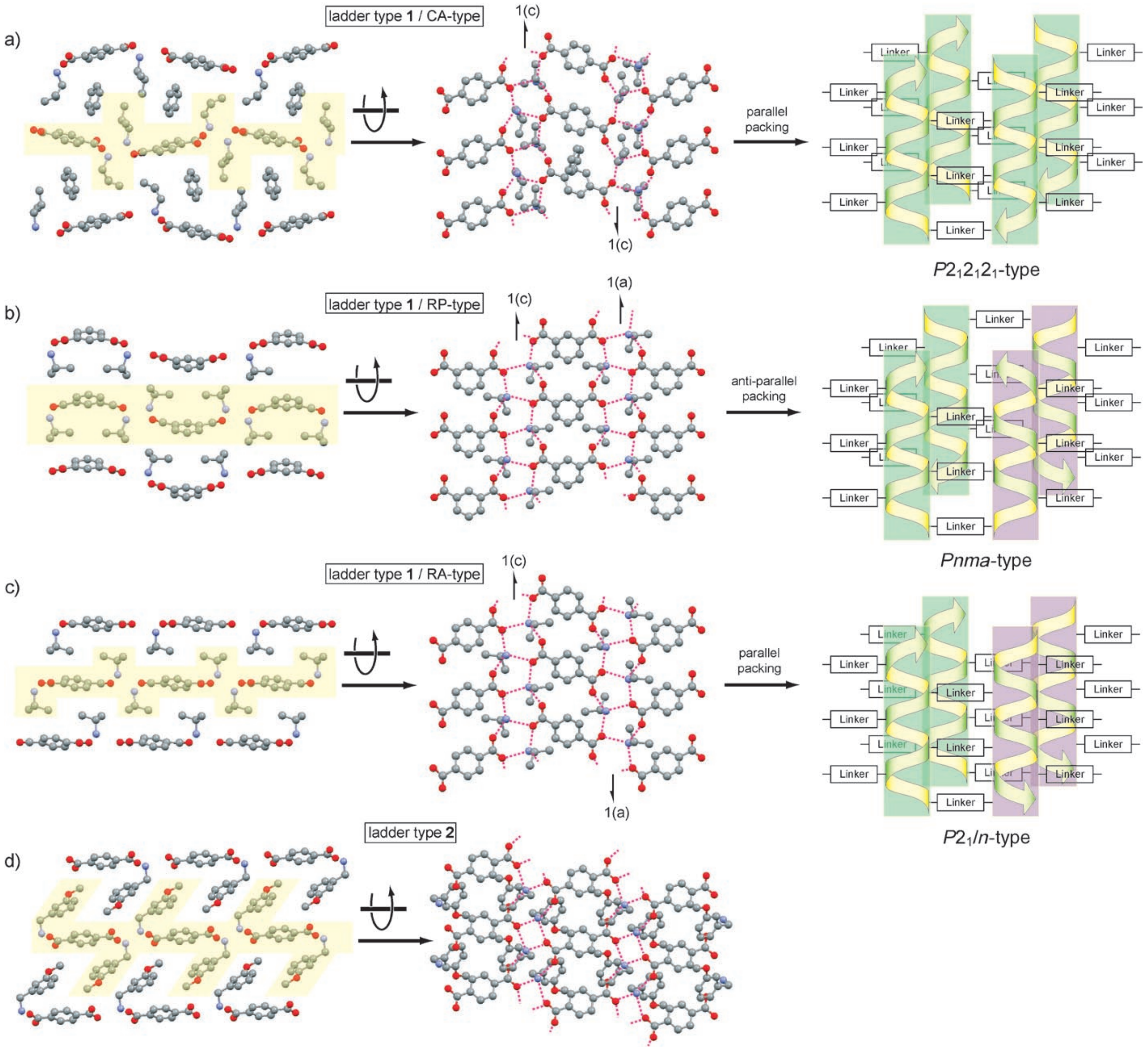


Figure 9. Packing diagrams of the crystal structures of a) **9a**, b) **5b**, c) **5a**, and d) **16a**. Carbon, nitrogen, and oxygen atoms are black, blue, and red, respectively. Hydrogen atoms are omitted for clarity.

gen bonds were observed, with retention of the ladder network.

Among *para*-substituted dicarboxylates other than terephthalic acid, most salts were of RA type. To facilitate further discussion of RA-type crystal structures (Figure 10), we determined the interlayer distances (d_{lay}), the intervals between helices bound by dicarboxylates (d_{car}), and the pitches of the helices (d_{pit}; Table 2). The bundles of helices varied in many ways depending on the substituents on the cations and the linkers in the anions. As the bulkiness of the substituent on the ammonium cation increased (isopropyl to benzhydryl), the interlayer distances increased from 6.3 to 10.5 Å. The distances between ammonium cations also varied depending on the dicarboxylic acid employed. In the case of terephthalic acid, the helices were arranged at almost the same period (nearly 10.5 Å) regardless of the bulkiness of the ammonium cations, whereas longer spacers resulted in elongation of d_{car} from 10.5 Å (*p*-phenylene) to 12.8 (2,6-naphthyl), 14.3 (4,4′-bisphenylene), and 16.3 Å (4,4′-azophenylene). Meanwhile, the pitches of the helices remained at around 6.3 Å. These results indicate that the structures of the assemblies may be easily tuned by varying the dicarboxylic acids and ammonium cations used.

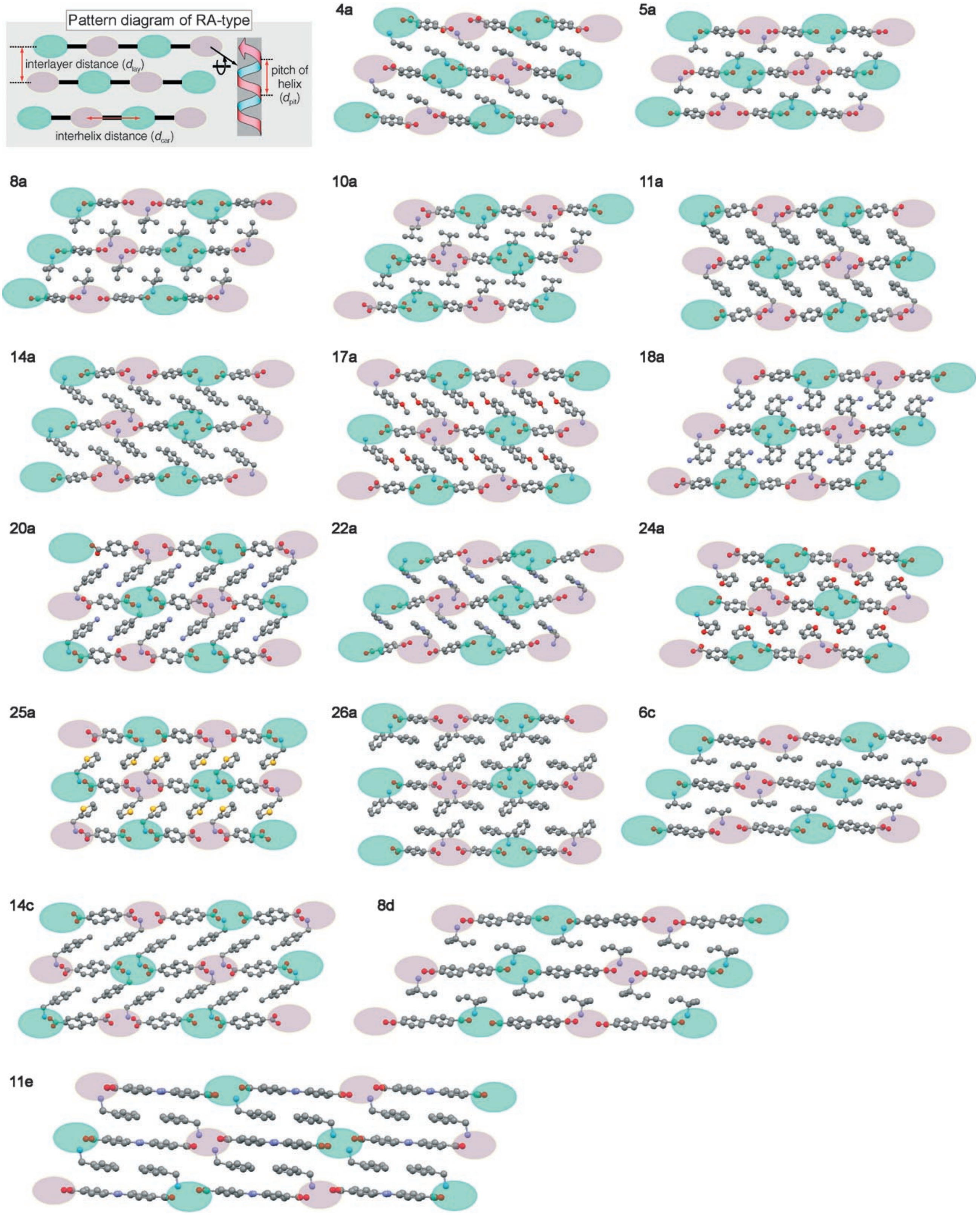


Figure 10. Pattern diagrams and crystal structures of RA-type salts **4a**, **5a**, **8a**, **10a**, **11a**, **14a**, **17a**, **18a**, **20a**, **22a**, **24a**, **25a**, **26a**, **6c**, **14c**, **8d**, and **11e**. Carbon, nitrogen, sulfur and oxygen atoms are black, blue, yellow, and red, respectively. Hydrogen atoms and methanol molecules included in the crystal of **11e** are omitted for clarity.

Table 2. Summary of the interlayer distances (d_{lay}), the intervals between helices bound by dicarboxylates (d_{car}), and the helix pitches (d_{pit}).

Salts	d_{lay} [Å]	d_{car} [Å]	d_{pit} [Å]
4a	6.930	9.790	6.133
5a	6.263	10.559	6.372
8a	7.293	10.592	6.440
10a	7.537	10.572	6.204
11a	7.695	10.427	6.317
14a	8.162	10.546	6.385
17a	8.641	10.681	6.039
18a	8.215	10.632	6.033
20a	7.894	10.720	6.248
22a	7.286	10.215	6.404
24a	7.148	10.091	6.054
25a	7.410	10.378	6.145
26a	10.516	10.440	6.320
6c	6.612	12.753	6.180
14c	7.801	12.425	6.467
8d	6.878	14.271	6.448
11e	6.209	16.261	6.449

Conclusion

We have demonstrated for the first time definitive supramolecular chirality in 1D ladder-type hydrogen-bond networks with enantiomeric helices. The chirality is based on the discrimination of two types of oxygen atom in the carboxylate anion as well as eight possible configurations of the ammonium cation. Based on these novel distinctions, a survey of the CSD resulted in the classification of six types of ladder-shaped hydrogen-bond network and seven types of 2_1-helical ladder network assembly, which included enantiomers. On the basis of these classifications, we constructed clay mimic structures with several bundle patterns by connecting the hydrogen-bond networks through bifunctional molecules. These studies not only provide a novel insight into discrimination in supramolecular assemblies and chirality from a different viewpoint to that of the graph set, but also result in constructive information that can be used for supramolecular synthon-directed crystal engineering. Furthermore, topological discussion of hydrogen-bond networks may provide a fresh viewpoint on hydrogen-bond-directed higher order structures.

Experimental Section

Materials: Reagents were purchased from Tokyo Chemical Industry. Single crystals were prepared by recrystallization from a mixture of methanol/acetonitrile or methanol/benzene.

Data collection: X-ray diffraction data were collected oby using a Rigaku R-AXIS RAPID diffractometer with a 2D area detector by using graphite-monochromatized $\mathrm{Cu_{K\alpha}}$ radiation ($\lambda = 1.54178$ Å). Direct methods, SIR92,[23] SIR2004,[24] and SHELXS97,[25] were used for structure solution. The structures were refined by a full matrix least-squares procedure with all of the observed reflections based on *F*.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions with isotropic displacement parameters relative to the connected non-hydrogen atoms, and not refined. Calculations were performed by using the TEXSAN[26] crystallographic software package, except for **6c**, **8c**, **9a**, **11e**, **14c**, and **17c**, which were calculated by using the CrystalStructure[27] crystallographic software package and SHELXL.[28]

Acknowledgements

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