

## Organic Layered Crystals with Adjustable Interlayer Distances of 1-Naphthylmethylammonium *n*-Alkanoates and Isomerism of Hydrogen-Bond Networks by Steric Dimension

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**Abstract:** A series of 1-naphthylmethylammonium *n*-alkanoates from acetate to triacontanoate produce isomorphic layered structures in the crystalline state. The interlayer distances, *d*-spacings, are proportional to the lengths of the alkyl chains. This is attributed to synergic intermolecular interactions;  $\pi$ - $\pi$  and CH- $\pi$  interactions of the naphthalene rings between the cations, hydrophobic interactions of the alkyl chains, and two-dimensional hydrogen-bond networks between the primary ammonium cations and the carboxylate anions. Salts made from carboxylic acids wider than 5.5 Å in the cross sections produce another columnar structure with a one-dimensional ladder-type hydrogen-bond network. Steric parameters of the acid components provide an explanation for the isomerism of the hydrogen-bond network.

### Introduction

Organic-inorganic hybrid layered crystals have been well-known as functional crystalline materials due to their restricted space for reactions and molecular recognitions as well as chemical and physical properties.<sup>1,2</sup> Their structures consist of two-dimensional (2D) inorganic networks made of covalent or ionic bonds and organic counterions or guest compounds sandwiched between them. The former components act as building blocks to construct robust layered structures, and the latter organic moieties act as adjustable components to tune the crystal structures and control the physical and chemical properties. The robustness of the former inorganic frameworks arranges the organic parts in a two-dimensional fashion. For example, the steric dimensions of the included organic components often adjust the interlayer distances (*d*-spacings or gallery heights)

between the inorganic layers.<sup>1</sup> The combination of these two functions attributable to the inorganic and organic components provides functional crystalline materials with tunable handles.

Recently, molecular designs of adjustable organic layered crystals by replacing inorganic 2D networks with robust organic layered structures have received considerable interest.<sup>3-7</sup> However, it is not easy to construct robust structures with weak intermolecular interactions, and only a few examples have ever been reported. Atwood and co-workers<sup>3</sup> first claimed an organic clay mimic based on the 2D array of calixarene derivatives, which was followed only by two elegant examples. Laminated crystalline materials of *N,N*-dialkylammonium salts of trimesic acid (1,3,5-benzenetricarboxylic acid) have been reported by

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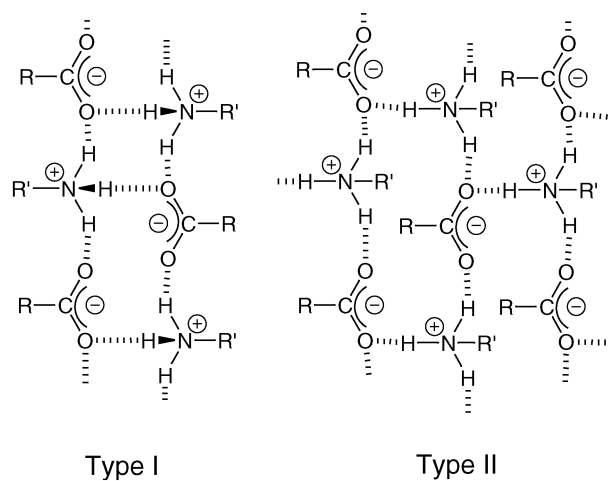
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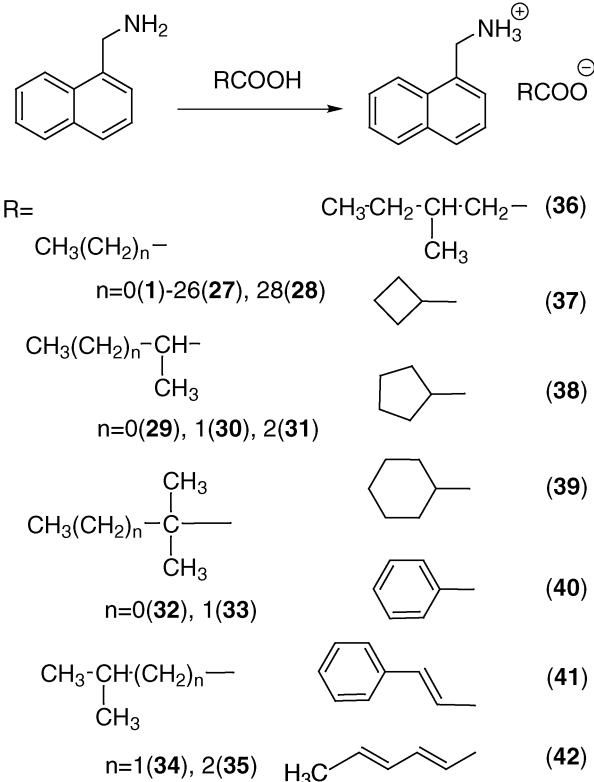
Zaworotko and co-workers,<sup>4</sup> and Ward and co-workers<sup>5</sup> demonstrated that 2D hydrogen-bond networks of guanidinium organosulfonates gave nanoporous layer structures with adjustable galleries by modifications of the bifunctional anions.<sup>5</sup> In this report, we describe the novel robust organic layered crystals with adjustable layer distances of the 1-naphthylmethylammonium *n*-alkanoates.

Carboxylate salts with organic amines have been widely used for the screening of functional organic crystalline materials, such as the optical resolutions of racemic acids or bases,<sup>8–10</sup> host–guest crystals,<sup>11</sup> crystalline-state photoreactions,<sup>12</sup> topochemical polymerizations,<sup>13</sup> and organogelators.<sup>14</sup> Salt formation has the following advantages: easy preparations without any skill for synthetic chemistry, systematic investigations based on a wide variety of combinations from commercially available acids and bases, and robust hydrogen bonds between polarized donors and acceptors. Many crystallographic studies had revealed that primary alkylammonium cations act as three-hydrogen-bond donors and carboxylate anions as one or more hydrogen-bond acceptors.<sup>10,12,13,15</sup> They mostly give the one-dimensional (1D) ladder-type hydrogen-bond network,<sup>10,13,15</sup> shown as type I, which arranges the substituent groups in a 1D direction to give a columnar structure. Recently, we reported another typical example of the hydrogen-bond network<sup>13</sup> (type II) for some carboxylate salts of substituted benzylamine and 1-naphthylmethylamine (NMA). They are suitable for the topochemical polymerizations of dienoic acids in the crystalline state.<sup>13</sup> The hydrogen-bond network spreads along two directions to provide

a bilayer structure similar to those of the inorganic layered crystals. More recently, we demonstrated that the CH– $\pi$  interaction supports the latter network of the 1-naphthylmethylamine salts.<sup>13e</sup> This prompted us to investigate the robustness of the type II hydrogen-bond network of the NMA salts as a function of the steric dimensions of the alkyl groups of the counter carboxylate anions. The scope and limitation of the robustness would clarify the role of the steric crowding for isomerism of the hydrogen-bond networks. Moreover, a series of *n*-alkanoic acids give us the robust layer structures with adjustable *d*-spacings as a function of the number of methylene groups, which is similar to the inorganic–organic hybrid layered crystals.<sup>12</sup>

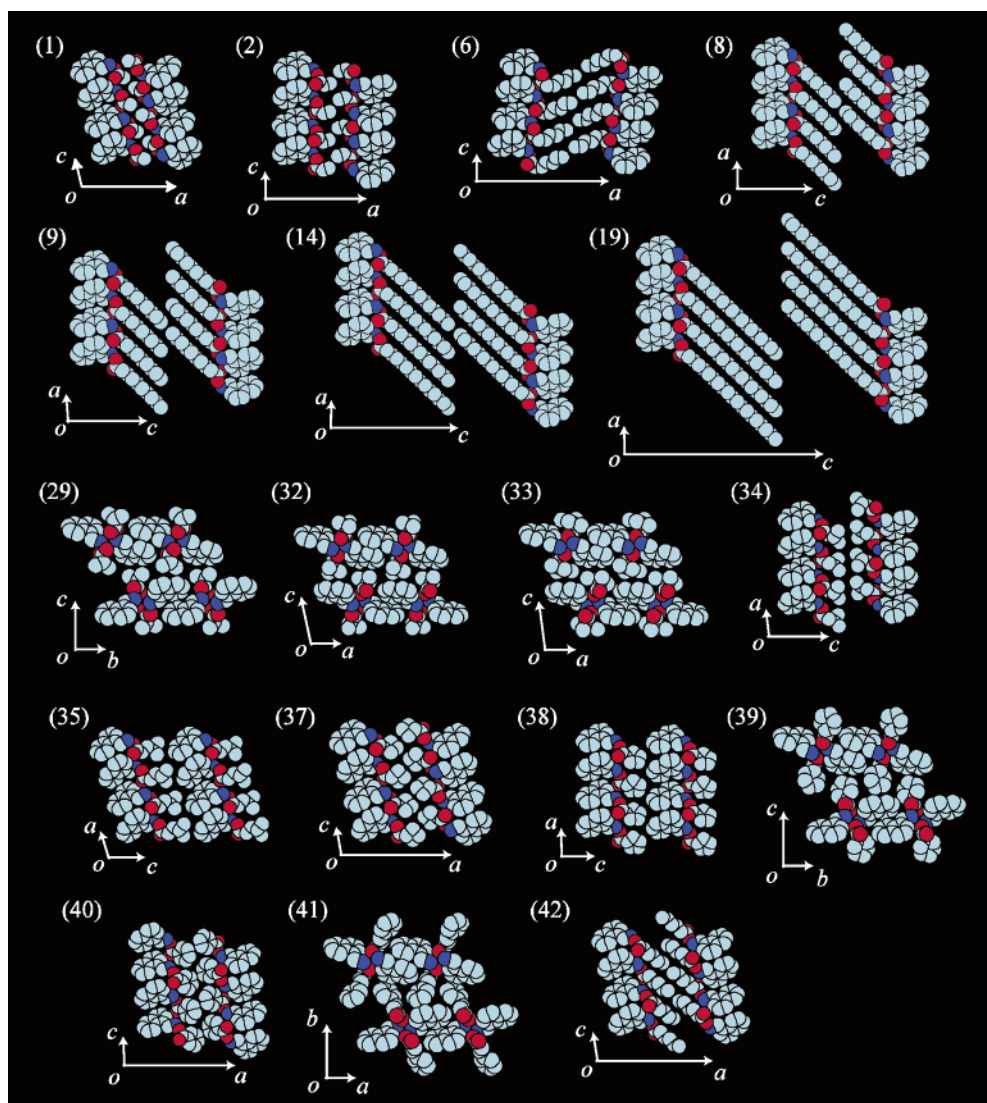


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## Experimental Section

**General Methods.** All chemicals and solvents were commercially available and used without any purification. The X-ray powder



**Figure 1.** Crystal structures of the compounds whose numbers are listed in parentheses. Hydrogen atoms are omitted for clarity. Gray, red, and blue circles represent carbon, oxygen, and nitrogen atoms, respectively.

diffraction (XRD) patterns were measured by a Rigaku RINT-1100 using graphite-monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) at room temperature. Salts were prepared by a previously reported method.<sup>13</sup>

**Crystal Structure Determinations.** The X-ray diffraction data were collected on a Rigaku R-Axis RAPID diffractometer with a 2D area detector using graphite-monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Lattice parameters were obtained by a least-squares analysis from reflections for three oscillation images. Direct methods (SIR92) were used for the structure solutions. The structures were refined by a full matrix least-squares procedure with all 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. All calculations were performed with the TEXSAN<sup>16</sup> crystallographic software package. The crystallographic parameters are summarized in the Supporting Information.

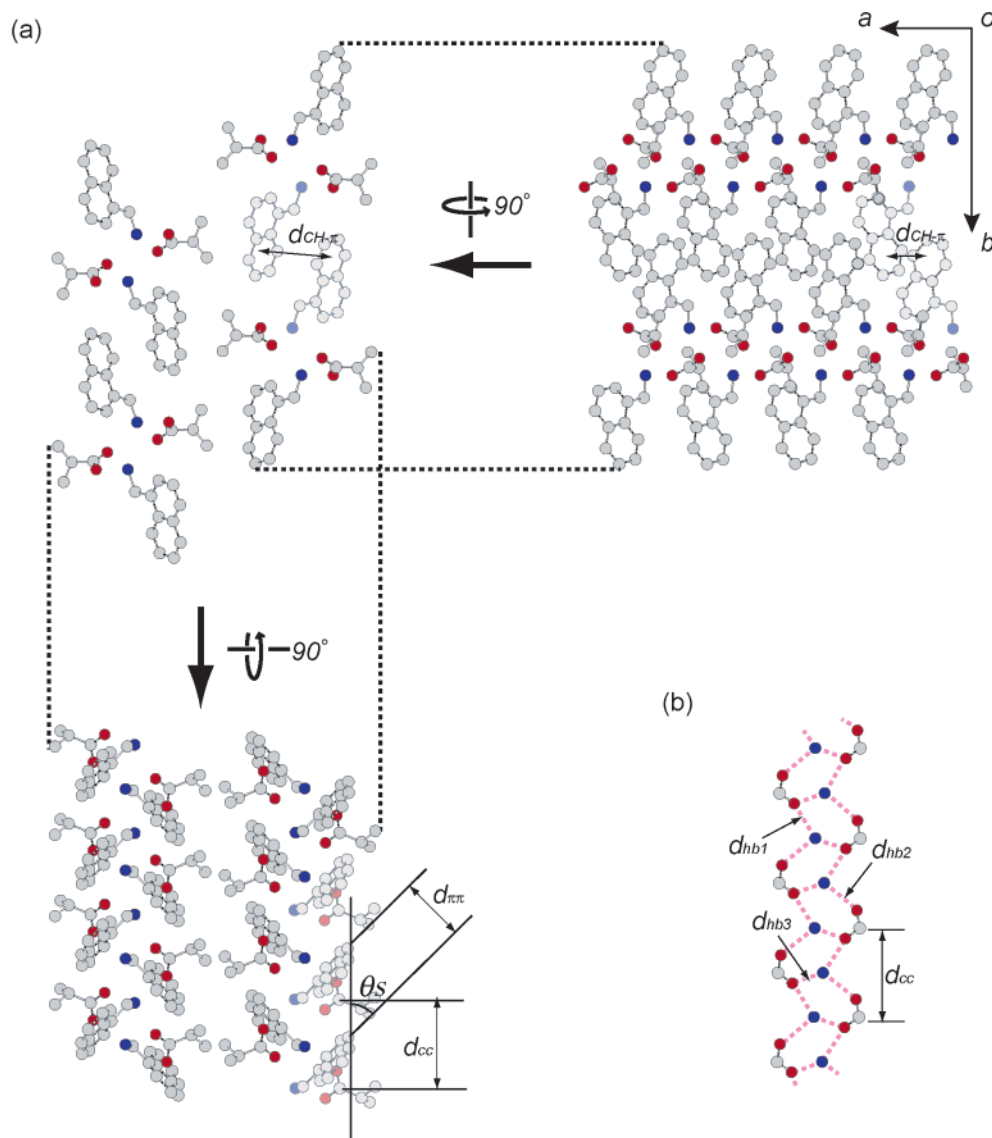
**Molecular Graphics.** The cross-sectional views of the carboxylate anions were prepared by using the plugin software MDL-Chime.<sup>17</sup> The atomic radii of hydrogen, carbon, nitrogen, and oxygen in the cross-sectional views are fixed at 1.20, 1.60, 1.50, and 1.45  $\text{\AA}$ , respectively.

## Results and Discussion

**Crystal Structures of NMA Salts.** Various NMA salts were prepared by mixing the corresponding carboxylic acid and NMA at a 1:1 molar ratio and recrystallized from various organic solvents to prepare single crystals for X-ray crystallography. Figure 1 shows the crystal structures of **1**, **2**, **6**, **8**, **9**, **14**, **19**, **29**, **32–35**, and **37–42**. They are classified into a layer structure with the 2D type II hydrogen-bond network and a columnar structure with the 1D type I hydrogen-bond network. The former is isostructural with that of the previously reported sorbate salt (**42**).<sup>13b</sup> A wide variety of carboxylic acids (**1**, **2**, **6**, **8**, **9**, **14**, **19**, **34**, **35**, **37**, **38**, and **40**), such as long aliphatic acids and

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**Figure 2.** (a) Packing diagram of the crystal structure of **29**; (b) hydrogen-bond network. Hydrogen atoms are omitted for clarity. Gray, red, and blue circles represent carbon, oxygen, and nitrogen atoms, respectively.

benzoic acid, form the layer type. The latter is new for the salts of NMA but ubiquitous for primary alkylammonium carboxylates.<sup>10,13,15</sup> A limited number of acids (**29**, **32**, **33**, **39**, and **41**) with two or more substituents at the  $\alpha$ -position construct the columnar type.

Packing diagrams of **29** viewed from three directions are shown in Figure 2 as a typical example of the columnar type. The hydrogen-bond distances and  $\pi$ - $\pi$  stacking parameters are summarized in Table 1. In this type, the ladder-type hydrogen-

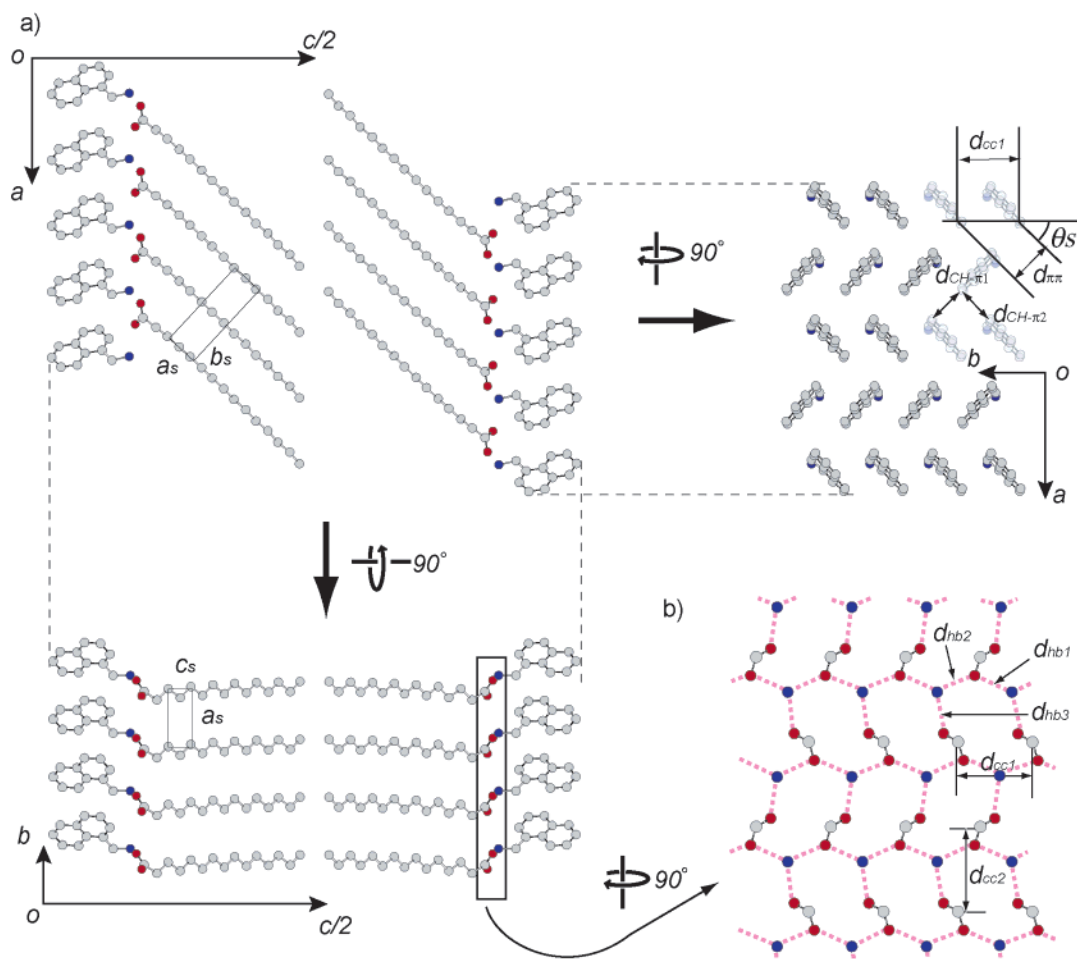
**Table 1.** Interplane Distances, Hydrogen-Bond Lengths, and Shearing Angles of the Aromatic Planes of the Columnar Structures<sup>a</sup>

	salts				
	29	32	33	39	41
$d_{hb1}$ (Å)	2.738	2.816	2.85	2.73	2.765
$d_{hb2}$ (Å)	2.639	2.669	2.703	2.71	2.676
$d_{hb3}$ (Å)	2.764	2.742	2.751	2.776	2.741
$d_{cc}$ (Å)	5.571	6.074	6.148	5.604	5.944
$d_{ch-\pi}$ (Å)	2.893	2.816	2.892	2.85	2.92
$d_{\pi\pi}$ (Å)	3.453	3.345	3.348	3.459	3.465
$\theta_s$ (deg)	51.57	56.76	57.63	51.52	54.37

<sup>a</sup> Interplane distances and hydrogen-bond lengths are denoted in Figure 2.

bond network (type I) runs along the crystallographic  $a$ -axis (Figure 2b). The alkyl groups of the anions and the naphthyl groups of the cations are arranged in the peripheral direction perpendicular to the network to reduce steric crowding between them. The  $a$ -axis is slightly longer for intracolumnar packing of the alkyl chains and stacking of the aromatic rings. Instead,

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**Figure 3.** (a) Packing diagram of the crystal structure of **14**; (b) hydrogen-bond network. Gray, red, and blue circles represent carbon, oxygen, and nitrogen atoms, respectively. Hydrogen atoms are omitted for clarity.

**Table 2.** Interplane Distances, Hydrogen-Bond Lengths, and Shearing Angles of the Aromatic Planes of the Layer Structures<sup>a</sup>

	salts												
	1	2	6	8	9	14	19	34	35	37	38	40	42
$d_{hb1}$ (Å)	2.808	2.808	2.881	2.780	2.784	2.815	2.791	2.841	2.791	2.755	2.829	2.748	2.832
$d_{hb2}$ (Å)	2.789	2.811	2.695	2.795	2.803	2.841	2.794	2.815	2.794	2.795	2.764	2.738	2.766
$d_{hb3}$ (Å)	2.735	2.749	2.868	2.745	2.725	2.754	2.771	2.754	2.771	2.768	2.757	2.821	2.787
$d_{cc1}$ (Å)	4.876	4.912	4.942	4.808	4.795	4.911	4.842	4.911	4.842	4.840	4.795	4.744	4.991
$d_{cc2}$ (Å)	5.576	5.639	5.551	5.622	5.623	5.641	5.681	5.641	5.681	5.756	5.767	5.884	5.613
$d_{ch-\pi 1}$ (Å)	2.925	2.973	2.880	2.887	2.896	2.935	2.834	2.978	2.834	2.964	2.947	2.976	2.846
$d_{ch-\pi 2}$ (Å)	2.734	2.768	2.790	2.708	2.716	2.755	2.779	2.817	2.770	2.785	2.714	2.733	2.822
$d_{\pi\pi}$ (Å)	3.480	3.464	3.197	3.391	3.483	3.487	3.438	3.626	3.438	3.485	3.491	3.524	3.550
$\theta_s$ (deg)	44.78	45.36	42.50	44.74	44.78	45.41	44.87	44.76	46.22	45.17	46.91	48.06	45.71

<sup>a</sup> Interplane distances and hydrogen-bond lengths are denoted in Figure 3.

intercolumnar CH- $\pi$  interactions between the aromatic rings produce bundles of the hydrogen-bonded columns, as shown in Figure 2.

On the other hand, the packing diagrams of **14** as a typical example for the common layer structures are depicted in Figure 3. They are constructed by alternative stacking of three segregated layers: a hydrogen-bonded (HB) layer, a naphthalene ring (Np) layer, and an alkyl (R) layer. The HB layer acts as an interface between the other two and produces a set of layers with the order of Np-HB-R. In principle, there are two types of stacking manners, head-to-tail (...//Np-HB-R//Np-HB-R//...) and head-to-head/tail-to-tail, (...//Np-HB-R//R-HB-Np//...) as structural isomerism, but most of them have the latter head-to-head/

tail-to-tail stacking. Only **35** and **38** provide the former type, as shown in Figure 1. The details of each layer explain the wide adaptation of the layer structures. The structural parameters including the hydrogen-bond distances and  $\pi$ - $\pi$  stacking are summarized in Table 2. First, in the HB layers, the primary ammonium cations and the carboxylate anions construct a 2D honeycomblike hydrogen-bond network (type II) as shown in Figure 3b. Three NHs of the primary ammonium cations form three hydrogen bonds (hb<sub>1</sub>, hb<sub>2</sub>, and hb<sub>3</sub>) with the three different carboxylate anions. The distances of the three hydrogen bonds are mostly in the range of the N-O hydrogen bonds. Second, in the naphthalene layers, the aromatic rings are arranged in a 2D fashion as shown in Figure 3. The shearing angles ( $\theta$ ) and

**Table 3.** Subcells for Alkyl Chain Packing in the Layer Structures<sup>a</sup>

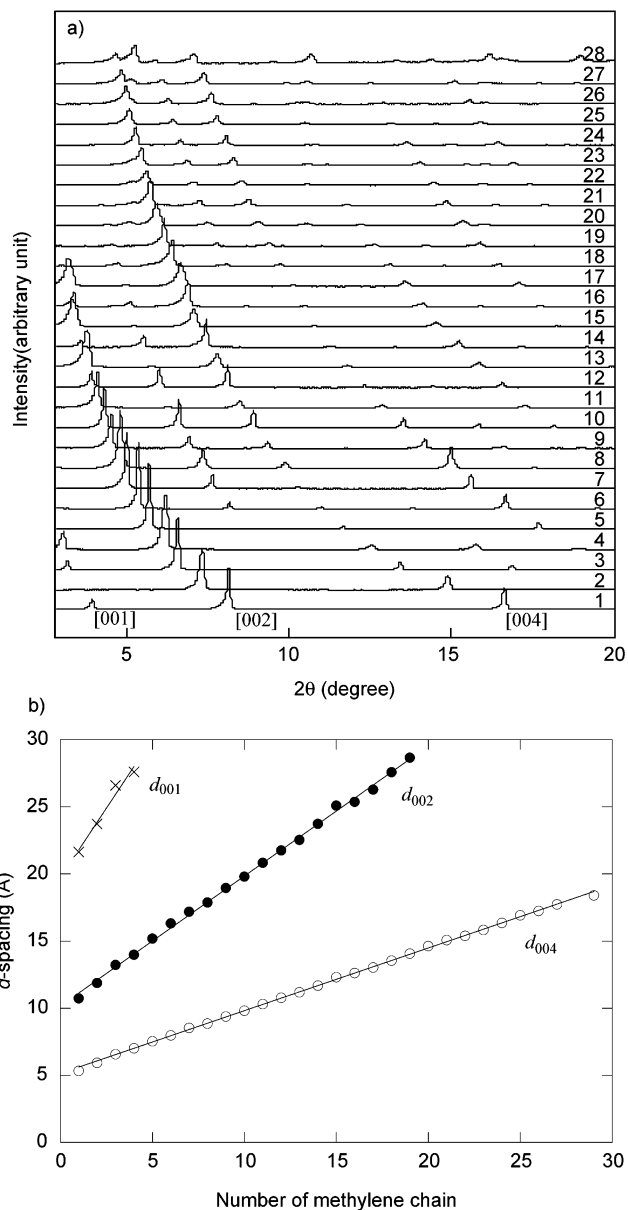
	salts				
	6	8	9	14	19
types	O <sub>1//</sub>	O <sub>1//</sub>	O <sub>1//</sub>	O <sub>1//</sub>	O <sub>1//</sub>
<i>a<sub>s</sub></i> (Å)	4.942	4.808	4.795	4.814	4.837
<i>b<sub>s</sub></i> (Å)	8.019	8.019	7.829	7.923	7.826
<i>c<sub>s</sub></i> (Å)	2.865	2.536	2.563	2.543	2.531
$\beta$ (deg)	94.1	94.1	94.4	92.1	91.9

<sup>a</sup> The subcell parameters are defined according to the previously reported method.<sup>19</sup>

interplanar distances ( $d_{\pi\pi}$ ) between the naphthalene rings are ca. 45° and 3.5 Å, respectively. According to the structural parameters, they are classified as  $\gamma$ -type structures among the four structural motifs of polyaromatic hydrocarbons.<sup>18</sup> This motif is suitable for both CH- $\pi$  and  $\pi$ - $\pi$  interactions and supports the two-dimensional hydrogen-bond network. Finally, in the alkyl layers, the anions construct the layer-type structure without interdigitations of the alkyl chains. This arrangement is one of the typical structural motifs of amphiphilic compounds, previously denoted as the bilayer type F structure.<sup>7</sup> Subcells of the alkyl chains are summarized in Table 3, and they are classified as distorted O<sub>1//</sub>-type packing.<sup>19</sup> These results indicate that the layer structures are composed of the innate robust molecular arrangements of individual intermolecular interactions. This should produce the robustness of the layer structures with a wide range of carboxylate anions.

**Layer Structures with Adjustable Spacing.** The robustness of the layer-type structures prompted us to investigate the correlation between the layer distances, *d*-spacings, and the length of the alkyl chain by powder X-ray diffraction, as shown in Figure 4a. It can be seen that all the salts (1–28) have similar XRD patterns and that the peaks are shifted to lower angles with increasing number (*n*) of methylene units of the alkyl chain. Plots of *n* versus interlayer distances (*d*) were investigated with the three diffractions ([001], [002], and [004]) marked in Figure 4b. They all have good linear correlations ( $d_{001} = 2.07n + 19.71$ ,  $r^2 = 0.9708$  for [001];  $d_{002} = 0.97n + 10.16$ ,  $r^2 = 0.9984$  for [002]; and  $d_{004} = 0.47n + 5.14$ ,  $r^2 = 0.9993$  for [004]). The slope of  $d_{002}$  agrees with a change in the size of one methylene group with a ca. 45° inclination, and interpolation (10.16 Å) to  $n = 0$  agrees with the summations of the naphthalene layer (7.2 Å) and the hydrogen-bond layer (3.4 Å) estimated from the crystal structures. In the series of *n*-alkanoate salts, there are no structural changes and the interlayer distances are changed continuously. This indicates that no apparent even–odd effects of the numbers of the alkyl chains on crystal packing are observed. This is in good contrast to those of the crystals of a series of  $\alpha$ -monofunctional or  $\alpha,\omega$ -difunctional alkanes.<sup>20</sup> This good linear correlation enables us to control the interlayer distances by changing the number of methylene groups of the fatty acids. This is attributed to the unique crystal structure of the NMA salts.

As described in the previous section, the layer structures of the NMA salts are constructed by alternative stacking of the three segregated layers and each layer is formed by weak interactions: hydrogen bonding,  $\pi$ - $\pi$ /CH- $\pi$  interactions, and alkyl chain packing. Extension of the alkyl chain length does

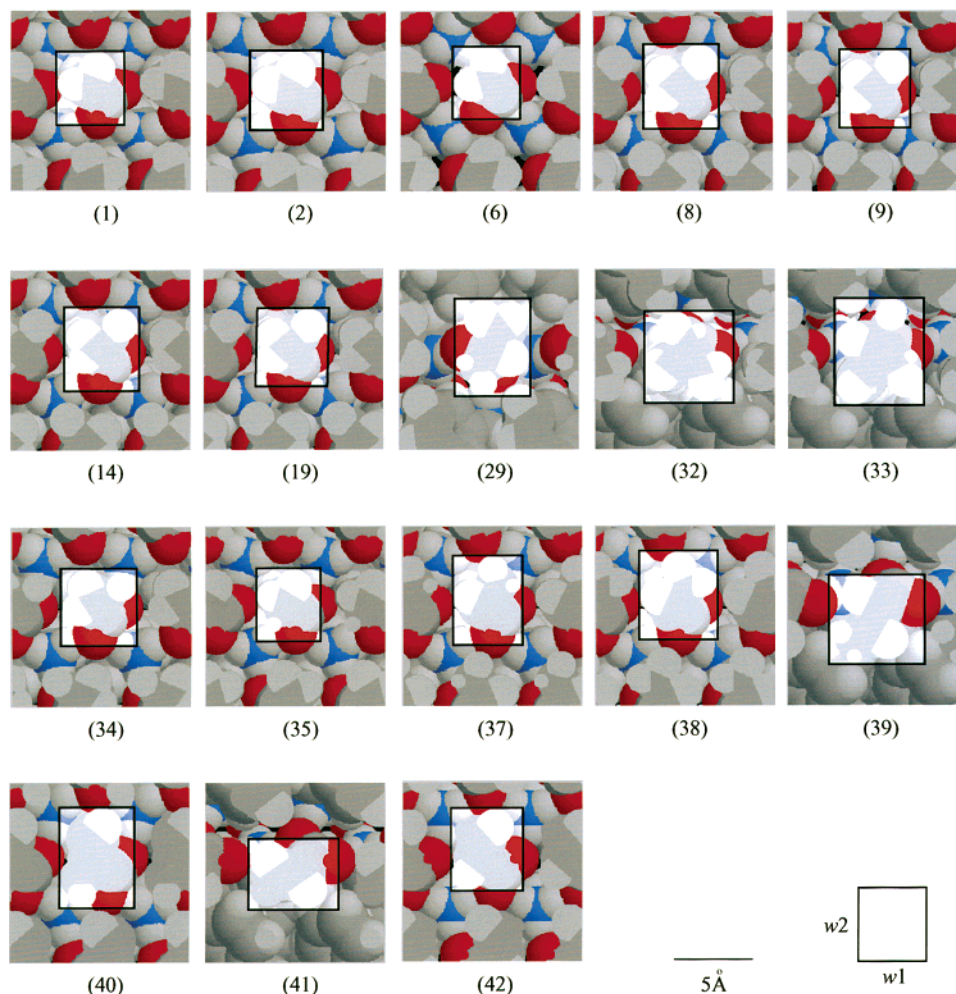


**Figure 4.** (a) XRD patterns of 1–28. (b) Plots of the methylene number (*n*) of the alkyl chains versus interlayer distances, (*d*).

not destroy these weak interactions, because the alkyl chains expand in the direction perpendicular to the layers. Therefore, no matter how the length of the alkyl chains changes, they can form the same layer structures. This is the reason all the fatty acid salts of NMA from acetate (1) to triacontanoate (28) construct the identical layer structures and the layer distances continuously change in proportion to the length of the alkyl chain.

**Columnar vs Layer.** To understand the isomerism of the hydrogen-bond networks, we estimated the steric dimensions [width (*w*<sub>1</sub>), height (*w*<sub>2</sub>)] of the alkyl groups of the carboxylate anions by slicing at the  $\alpha$ -carbon of the carboxylate anions parallel to the plane made by the nitrogen atoms in the hydrogen-bond network for the layer-type crystals. On the other hand, in the columnar structures, they are defined by the cross sections that sliced along the direction parallel to the  $\pi$ - $\pi$  stacking of the naphthalene rings. Cross sections of the alkyl groups are shown in Figure 5, and Table 4 summarizes the steric dimensions

(20) For examples see (a) Boese, R.; Weiss, H.-C.; Bläser, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 988. (b) Thalladi, V. R.; Boese, R.; Weiss, H.-C. *Angew. Chem., Int. Ed.* **2000**, *39*, 918. (c) Thalladi, V. R.; Nüsse, M.; Boese, R., *J. Am. Chem. Soc.* **2000**, *122*, 9227.



**Figure 5.** Cross-sectional views of the substituents of the carboxylate anions of the compounds whose numbers are listed in parentheses. The brighter boxed area in each figure shows one carboxylic acid in the cross sections. White, gray, red, and blue circles represent hydrogen, carbon, oxygen, and nitrogen atoms, respectively.

**Table 4.** Widths ( $w1$ ), Heights ( $w2$ ), and Areas for Alkyl Groups of Carboxylate Anions<sup>a</sup>

	salts								
	1	2	6	8	9	14	19	29	32
$w1$ (Å)	4.15	3.85	4.05	4.35	4.35	4.8	4.4	4.25	5.7
$w2$ (Å)	4.75	4	4.45	5.15	5	5.07	5	5.8	5.7
area (Å <sup>2</sup> )	19.71	15.4	18.02	22.4	21.75	24.34	22	24.65	32.49
type <sup>b</sup>	L	L	L	L	L	L	L	C	C
	salts								
	33	34	35	37	38	39	40	41	42
$w1$ (Å)	5.4	4.7	4.05	4.5	4.75	5.7	4.2	5.5	4.45
$w2$ (Å)	6.55	4.95	4.8	4.95	5.3	5.2	6.15	4.3	5
area (Å <sup>2</sup> )	35.37	20.45	19.44	22.28	25.18	29.64	25.83	23.65	22.25
type <sup>b</sup>	C	L	L	L	L	C	L	C	L

<sup>a</sup> Estimated by cross-sections. <sup>b</sup> Structural motifs in crystalline state: L, layer type; C, columnar type.

estimated from the cross-sections. If both  $w1$  and  $w2$  are less than 5.5 Å, the salts have the layer structures. Otherwise, the columnar structures are formed in the NMA salts. The metric comparison between the steric dimensions ( $w1$ ,  $w2$ ) and the repeating distances of the hydrogen-bond network explains this structural isomerism of the hydrogen-bond networks. The crystallographic parameters indicate that the repeating distances of the functional groups in the layer structure are 4.8–5.0 Å

and 5.4–5.6 Å along the two-dimensional hydrogen-bond network. In the columnar type structures, the hydrogen-bonding repeating distances are 5.6–6.2 Å, which is longer than those of the layer structures. When either  $w1$  or  $w2$  exceeds the longer hydrogen-bond distance (5.4–5.6 Å) of the layer structures, the salts provide the columnar structures. In the case of the benzoate salt (**40**), the planar benzene ring is thin enough ( $w1 = 4.2$  Å) and just fits in the layer structures. This indicates that the steric bulkiness of the functional groups on the carboxylate anions plays an important role in the robust layer structures. Exceeding the upper limit in width or height isomerizes the hydrogen-bond network from type II to type I. This result supports the fact that the steric crowding reduces the dimensionality of the hydrogen-bond networks.<sup>21</sup> Therefore, metric comparisons between the steric dimensions of the alkyl groups and repeating distances of the hydrogen-bond networks provide an insight for the prediction of the robustness and isomerism of the structural motifs in the crystalline state.

**Conclusion.** We demonstrated the robust layer structures of NAM salts and the structural isomerism of the hydrogen-bond network. In the layer structure, the characteristic structural motifs

(21) Control of crystal structures of peripheral crowding, for examples see Whitesides, G. M.; Simank, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37–44.



of the individual intermolecular interactions provide the robustness of the crystal structures. This is attributed to agreement of the repeating distances among the three supramolecular synthons. In particular, we demonstrated synergy of the steric dimensions of the alkyl groups and the repeating distances of the hydrogen-bond networks within the robust layered crystal structures. Therefore, understanding the steric dimensions, geometries of interactions, and characteristic repeating distances of the supramolecular synthons is essential for elucidating the crystal structures from molecular structures, designing robust structural motifs, and predicting isomerism of the hydrogen-bond networks.<sup>22</sup>

Moreover, this system provides unique organic robust layer structures with adjustable interlayer spacing controlled by the number of methylene units. The linear relationship from C1 to C29 is rare for organic crystalline materials<sup>3–7</sup> but ubiquitous in the organic–inorganic hybrid layered crystals.<sup>1</sup> The controlled two-dimensional array would provide us the various functions

such as ion exchange, chemical reactions, and molecular recognitions.

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**Supporting Information Available:** Table of X-ray crystallographic studies (PDF) and files of new crystal structures (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (22) Examples of adjustments of the two or more intermolecular interactions in crystalline state, see (a) Lewis, F. D.; Yang, J.-S.; Stern, C. L. *J. Am. Chem. Soc.* **1996**, *118*, 12029. (b) Swift, J. A.; Pal, R.; McBride, J. M. *J. Am. Chem. Soc.* **1998**, *119*, 996. (c) Mascal, M.; Hansen, J.; Fallon, P. S.; Blake, A. J.; Heywood, B. R.; Moore, M. H.; Turkenburg, J. P. *Chem. Eur. J.* **1999**, *5*, 381. (d) Schauer, C. L.; Matwey, E.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 10245. (e) Nguyen, T. L.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 11057.