

Hydrogen-Bond Networks of Mellitate Anions ($[C_6(COO)_6H_{6-n}]^{n-}$) in Salts with Pyridine Derivatives

Norihito Kobayashi, Toshio Naito, and Tamotsu Inabe*

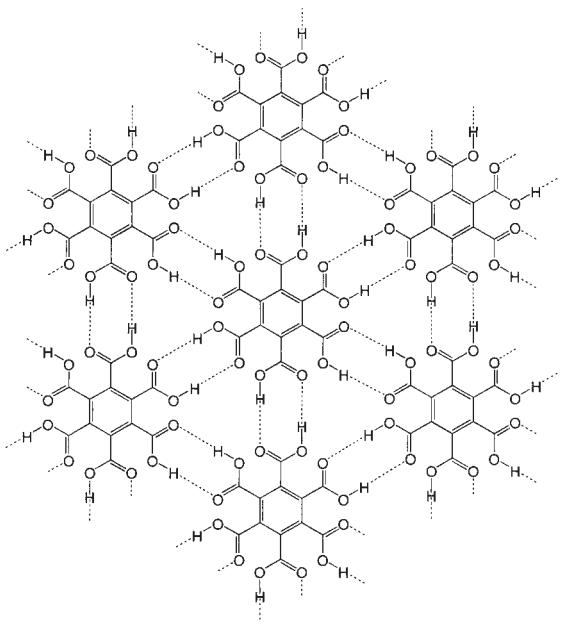
Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810

(Received January 24, 2003)

Single crystals of mellitate anion ($[C_6(COO)_6H_{6-n}]^{n-}$) salts with 3-aminopyridinium, $[3\text{-}NH_2C_5H_4NH^+]_3[C_6(COO)_6H_3^{3-}]$ (**1**), 4-methylpyridinium, $[4\text{-}CH_3C_5H_4NH^+]_2[CH_3C_5H_4N]_2[C_6(COO)_6H_4^{2-}]$ (**2**), $[4\text{-}CH_3C_5H_4NH^+]_2[C_6(COO)_6H_4^{2-}]\cdot 2CH_3OH$ (**3**), pyridinium, $[C_5H_5NH^+]_2[C_6(COO)_6H_4^{2-}]\cdot 2H_2O$ (**4**), 3-methylpyridinium, $[3\text{-}CH_3C_5H_4NH^+]_2[C_6(COO)_6H_4^{2-}]$ (**5**), $[3\text{-}CH_3C_5H_4NH^+]_5[C_6(COO)_6H_3^{3-}][C_6(COO)_6H_4^{2-}]\cdot CH_3OH$ (**6**), and isoquinolinium, $[C_9H_7NH^+]_2[C_6(COO)_6H_4^{2-}]\cdot CH_3OH$ (**7**), $[C_9H_7NH^+]_2[C_9H_7NH_{0.5}^{0.5+}][C_6(COO)_6H_{3.5}^{2.5-}]\cdot CH_3OH$ (**8**) have been structurally characterized. In these crystals, strong hydrogen-bonds between the mellitate anions are formed. Various arrangements that depend on the deprotonation number, n, have been found. All hydrogen-bonds found between the anions are combinations of a carboxy and a carboxylato group. The "triangular hydrogen-bond" unit between the anions, in which three anions are connected by the three hydrogen-bonds to form a triangle, in the salt with $n = 3$, induces the two dimensional (2-D) sheet self-organizing structure in this crystal. "Dual hydrogen-bond" units between the anions, in which two pairs of the hydrogen-bonds connect the neighboring anions, have been found in the salts with $n = 2$ or 2.5. The repetition of the co-planer "dual hydrogen-bond" induces the anion one-dimensional (1-D) belt structure, while the combination of the standing and co-planer "dual hydrogen-bond" units induces the 2-D grid structure. These 2-D grids are further linked by hydrogen-bonds to form a channel. In all the salts ($n = 3$, 2, 2.5), the counter cation molecules are arranged in the space defined by the anion network.

The molecules possessing several functional groups at the regulated positions are promising components for the supramolecular chemistry or crystal engineering.[1] The functional groups are utilized for assembling the components by attractive interactions such as hydrogen-bonds, coordination bonds, and electrostatic forces. Among them, hydrogen-bonds are the most investigated intermolecular interaction; in particular, the carboxy group is often used to create hydrogen-bond networks for the association of the molecules. The hydrogen-bonding patterns of carboxylic acids (especially, the aromatic carboxylic acids) are well investigated, and they are utilized for the formation of various supramolecular architectures.[2] It is known that neutral trimesic acid (benzene-1,3,5-tricarboxylic acid) molecules form honeycomb hydrogen-bond networks in its crystal,[3] and the size of the hexagonal cavities could be regulated by the spacer molecules.[4] In the salts of pyromellitic acid (benzene-1,2,4,5-tetracarboxylic acid) anion with some pyridiniums, the anions aggregate spontaneously, and form a multi-dimensional network by the hydrogen-bonds between the carboxy (carboxylato) groups.[4a,5]

On the other hand, the analogue mellitic acid (benzenehexacarboxylic acid) is known to form a two-dimensional (2-D) sheet in which all of the carboxy groups participate in hydrogen-bonds (Scheme 1).[6] The analogue is expected to form the symmetric hydrogen-bond network of the partially deprotonated carboxylate anions $[C_6(COO)_6H_{6-n}]^{n-}$, where n is the number of protons dissociated from the mellitic acid. When n is small, the mellitate anions are expected to form multiple hydrogen-bonds with neighboring anion molecules. If such anions with self-organizing ability form a network, the counter ionic components can be packed within the space defined by them. Since the physical properties of molecular crystals are strongly dependent on the molecular arrangement and intermolecular interactions, such a regulation of packing may be useful for the functionalized cationic molecules to be arranged in a regulated way. However, crystals of mellitic acid or mellitate anion so far reported are not the salts or co-crystals with



Scheme 1.

Published on the web July 15, 2003; DOI 10.1246/bcsj.76.1351

organic molecules but the metal complexes with large n ($n \geq 4$).[7] In some of the complexes, hydrogen-bonds between the anions were observed,[7h–j] but their self-organizing properties are little known.

In order to investigate the formation of hydrogen-bonds between mellitate anions with small values of n (1–3), we have examined the structures of the salts with pyridine derivatives. They are advantageous from the following reasons: the pK_a values of the pyridinium derivatives correspond to the pK_a values for the partial deprotonation of the mellitic acid ($n = 1$–5), single crystal specimens with sufficient qualities for X-ray analyses are available, and the pyridine ring is geometrically sensitive to the proton position. Also, pyridines can act as a proton acceptor and pyridiniums as a proton donor for the hydrogen-bond formation that may interfere with the network formation of the mellitate anions, so that we can deduce the strength of the self-organizing ability of the mellitate anions from the resultant crystal structures.

As a result of crystallization, eight colorless crystals [$n = 3$ (**1**), $n = 2$ (**2**, **3**, **4**, **5**, and **7**), and $n = 2.5$ (**6** and **8**)] have been obtained. All of the n values are less than 4. In this paper we describe the structures of these salts and the relationships found between the n value and the molecular arrangement pattern in these salts.

Results

Structural Features of the Deprotonation and Protonation. The determination of the hydrogen positions would be critical to obtain information about n. However, it is difficult to determine the hydrogen positions solely from the electron densities obtained by the X-ray diffraction data. In this paper, we utilized the following geometric features that appeared when a proton is bound to some specific atoms in addition to the electron density information.

a. Carboxy (Carboxylato) Group: When a proton is bound to the carboxylato group, one C–O bond bound to the proton should become longer than the other. In a very asymmetrical carboxy group, therefore, the protonated oxygen can be determined without ambiguity.[7i] For the hydrogen-bond between the carboxy and carboxylato groups, there may be an intermediate state in which one proton is nearly equally shared by the two groups. In order to investigate such a systematic change in the geometry, we have adopted the ratio ($r = a/b$, $a \geq b$) of two C–O bond lengths in the $-CO_aO_b$ group, and plotted it using 89 neutron diffraction data sets of carboxy groups and/or carboxylato groups in the Cambridge Structural Database (CSD)[8] in Fig. 1(a). Based on the determined hydrogen position, the r values can be classified into three regions. When the $-CO_aO_b$ group is not bound to a hydrogen, that is a carboxylato group, r is smaller than about 1.03. When r is larger than that, the hydrogen forms a covalent bond with O_a, corresponding to a carboxy group. This region can be further classified into two regions. Fig. 1(b) shows the relationship between the r value and the O···O distance in hydrogen-bonds between the carboxy and carboxy/carboxylato groups [part of the data in Fig. 1(a)]. One can see three areas: I, II, and III. When the O···O distance is very short (<2.49 Å) (area III), the hydrogen atom is equally shared by both of the oxygen atoms and is often on a symmetry

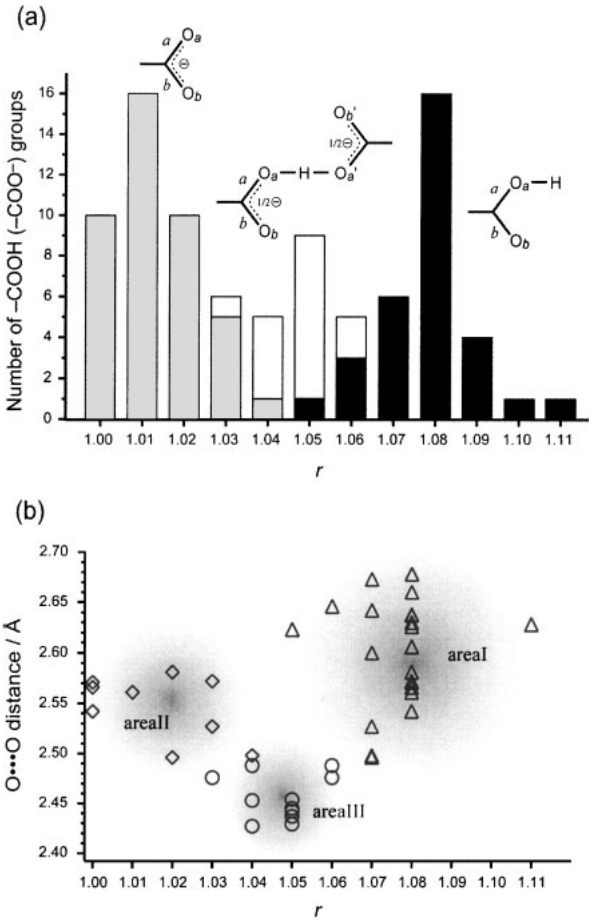


Fig. 1. a) Hystgram of the ratio (r) of the two C–O bond lengths in carboxy (carboxylato) groups. b) Relationship between the r value and the O···O distance. The data are taken from CSD.[8]

element. Since the r value in area III has some overlap not only with area I (carboxy group) but also with area II (carboxylato group), we adopted both r values and O···O distances for determining the hydrogen-bond structure.

b. Pyridine (Pyridinium) Ring: Recently, Steiner reported about the relationship between the C–N–C bond angle of the pyridine (pyridinium) ring and the N···O distance in N···H···O hydrogen-bond in 4-methylpyridine containing compounds; when the O–H···N hydrogen bond becomes shorter, the C–N–C bond angle is gradually widened, and the hydrogen-bond structure switches to the N^+–H···$^-$O type at the critical angle of about 120°.[9] We have performed the similar analysis using 19 neutron diffraction data sets containing pyridine or pyridinium in the Cambridge Structural Database (CSD). Figure 2 shows that, when the nitrogen is not bound to hydrogen, the C–N–C bond angle of the pyridine framework is smaller than about 119.4°. When a proton is bound to the nitrogen, namely pyridinium, the angle becomes larger than that. Especially in very short N···H···O hydrogen-bonds (N···O; ~2.52 Å), the C–N–C bond angle situates in the narrow region around 119.7°, and the hydrogen is bound to both N and O. Thereby, in our structure analyses, a hydrogen atom was fixed at the ideal position as pyridinium when the C–N–C angle is

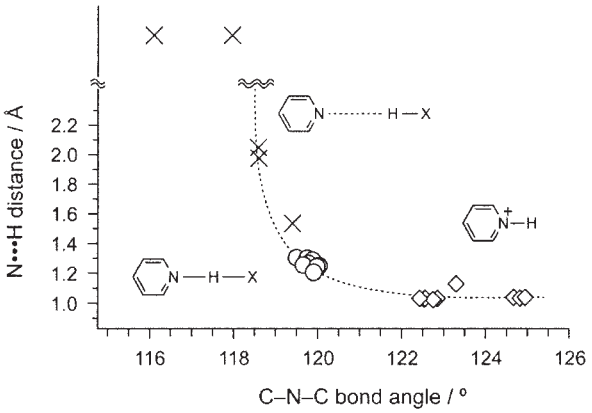
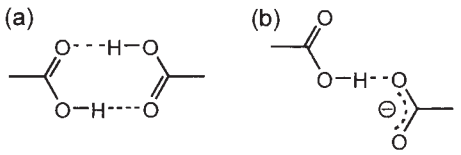


Fig. 2. Relationship between the C–N–C bond angle in the pyridine ring and the N···H distance. The dotted line is a guide for eyes. The data are taken from CSD.[8]



Scheme 2.

sufficiently wider than 120°. When the angle is smaller than 119°, we can assume that no covalent bond is formed between N and H. In the case of the intermediate angle region, a hydrogen atom was fixed at the position determined from the difference Fourier map.

Modes of Hydrogen-bonds. In all the crystals studied here, the mellitate anions form intermolecular hydrogen-bonds with each other. Though the mellitate anion ($n = 2$–3) has both carboxy and carboxylato groups, none of the hydrogen-bonds in these crystals are the "paired hydrogen-bond" type formed between the carboxy groups, as often found in crystals composed of neutral carboxylic acids. The hydrogen-bonds between the mellitate anions are entirely the "single hydrogen-bond" type formed between the carboxy group and the carboxylato group (Scheme 2).

The pyridinium (pyridine) ring also forms hydrogen-bonds with the carboxylato (carboxy) group. There are two modes of hydrogen-bonds: one N–H group bridges two carboxylato (carboxy) groups, "Type 1" (bifurcated hydrogen-bond); and one N–H group forms hydrogen-bond with only one carboxylato (carboxy) group, "Type 2". In the Type 1 hydrogen-bonds, the N···O distances are relatively long, while the Type 2 hydrogen-bonds are generally strong and the N–H···O (N···H–O) alignment is almost linear.

$[3\text{-}NH_2C_5H_4NH^+]_3[C_6(COO)_6H_3^{3-}]$ ($n = 3$) (1). The geometries of six independent carboxy (carboxylato) groups (A to F as shown in Fig. 3) in the mellitate anion are summarized in Table 1. In the crystal, there are three pairs of hydrogen-bonds between the carboxy (carboxylato) groups; A···F^{i}, B···E^{ii}, and C···D^{iii}. Among them, A···F^{i} and B···E^{ii} are very strong hydrogen-bonds, and the O···O distances are shorter than 2.5 Å (hydrogen-bond distances and their symmetry operations between mellitate anions for all the compounds are summarized in Table 2). The short hydrogen-bond distances

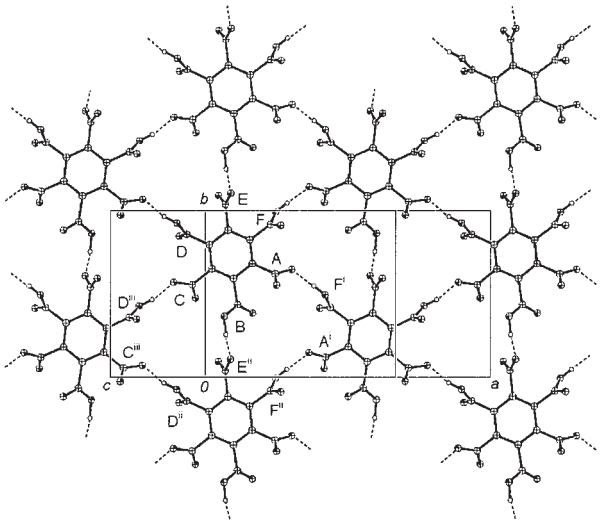


Fig. 3. 2-D sheet of the mellitate anions ($n = 3$) in **1**.

and their r values of A, B, E, and F (1.04–1.07) indicate that one proton locates nearly midway between the two –COO groups [as shown in Fig. 1(b)]. On the other hand, the r values in the C···D^{iii} pair indicate that D is a carboxy group and C is in the intermediate region, though the O···O distance is not very short. Since it can be seen that all the 3-aminopyridine molecules become the pyridinium cations from the very large C–N–C bond angles (θ1, θ2, and θ3 indicated in Fig. 4 and Table 1), C must be a carboxylato group based on the stoichiometry. The difference Fourier map also supports this assignment.

The strong O···O interactions make $[C_6(COO)_6H_3^{3-}]$'s arrange into a 2-D sheet in the *ab* plane (Fig. 3). N(11) of 3-aminopyridinium forms a Type 2 hydrogen-bond with C, and N(21) and N(31) form Type 1 hydrogen-bonds with A and F and with B and E^{ii}, respectively (Fig. 4) [for all compounds, hydrogen-bonds and their distances (Å) (except between anions) are indicated in each figure]. The amino groups also form hydrogen-bonds with $[C_6(COO)_6H_3^{3-}]$, but these are weak (2.90–3.21 Å).

The anion planes are not parallel to the sheet, and are arranged stepwise (Fig. 5). The cation molecules are packed between the 2-D sheets of $[C_6(COO)_6H_3^{3-}]$ by the N–H···O and N^+–H···O hydrogen-bonds. The arrangement of cations viewed along the *c* axis is a herringbone type, and the molecular plane is almost perpendicular to the anion sheet.

$[4\text{-}CH_3C_5H_4NH^+]_2[4\text{-}CH_3C_5H_4N]_2[C_6(COO)_6H_4^{2-}]$ ($n = 2$) (2). The mellitate anion is on a two-fold axis, and the geometries of three independent carboxy (carboxylato) groups (A, B, and C; shown in Fig. 6) are summarized in Table 1. The r values clearly indicate that A and C are carboxy groups, and that B is a carboxylato group. The C–N–C bond angles (θ1 and θ2) of the pyridine (pyridinium) rings show that N(1) is not bound to a proton, and that N(2) is protonated. So the formula of **2** is $[4\text{-}CH_3C_5H_4NH^+]_2[4\text{-}CH_3C_5H_4N]_2[C_6(COO)_6H_4^{2-}]$ ($n = 2$).

Two carboxy-carboxylato pairs of hydrogen-bonds, B···C^{i} and C···B^{i}, link the two neighboring $[C_6(COO)_6H_4^{2-}]$ molecules, and this leads to the formation of a one-dimensional (1-

Table 1. C–O Bond Lengths, r in Mellitate Anions, and C–N–C Bond Angles in Pyridinium (Pyridine) Rings

	Carboxy (carboxylato) group	a/Å	b/Å	r	C–N–C bond angle/°	
1	A	1.298(3)	1.217(3)	1.07	$\theta1$	123.8(2)
	B	1.299(3)	1.215(3)	1.07	$\theta2$	124.3(2)
	C	1.275(3)	1.230(3)	1.04	$\theta3$	124.1(2)
	D	1.316(3)	1.206(3)	1.09		
	E	1.281(3)	1.227(3)	1.04		
	F	1.286(3)	1.225(3)	1.05		
2	A	1.302(2)	1.215(2)	1.07	$\theta1$	118.3(2)
	B	1.251(2)	1.248(2)	1.00	$\theta2$	120.9(2)
	C	1.313(2)	1.212(2)	1.08		
3	A	1.250(3)	1.247(4)	1.00	$\theta1$	121.6(3)
	B	1.314(4)	1.209(4)	1.09	$\theta2$	122.3(6)
	C	1.263(4)	1.241(4)	1.02		
	D	1.305(4)	1.213(4)	1.08		
	E	1.309(4)	1.217(4)	1.08		
	F	1.317(3)	1.207(4)	1.09		
4	A	1.314(3)	1.213(3)	1.08	$\theta1$	121.9(2)
	B	1.308(3)	1.221(3)	1.07		
	C	1.273(3)	1.240(3)	1.03		
5	A	1.297(2)	1.220(2)	1.06	$\theta1$	120.9(2)
	B	1.303(2)	1.214(2)	1.07	$\theta2$	122.7(2)
	C	1.331(2)	1.201(2)	1.11		
	D	1.256(2)	1.255(2)	1.00		
	E	1.317(2)	1.209(2)	1.09		
	F	1.277(2)	1.228(2)	1.04		
6	A1	1.260(4)	1.244(5)	1.01	$\theta1$	122.8(4)
	B1	1.315(4)	1.206(4)	1.09	$\theta2$	123.2(6)
	C1	1.290(4)	1.212(4)	1.06	$\theta3$	120.1(6)
	D1	1.304(4)	1.209(4)	1.08	$\theta4$	122.9(4)
	E1	1.312(4)	1.210(4)	1.08	$\theta5$	126.1(5)
	F1	1.271(4)	1.236(5)	1.03		
	A2	1.281(4)	1.220(4)	1.05		
	B2	1.319(4)	1.199(4)	1.10		
	C2	1.279(4)	1.235(4)	1.04		
	D2	1.318(4)	1.201(4)	1.10		
	E2	1.310(4)	1.209(4)	1.08		
	F2	1.278(4)	1.229(4)	1.04		
7	A	1.281(4)	1.236(4)	1.04	$\theta1$	121.1(3)
	B	1.320(4)	1.212(4)	1.09	$\theta2$	122.7(3)
	C	1.295(4)	1.208(4)	1.07		
	D	1.318(4)	1.216(4)	1.08		
	E	1.261(4)	1.244(4)	1.01		
	F	1.318(4)	1.204(4)	1.09		
8	A	1.260(4)	1.237(4)	1.02	$\theta1$	122.2(3)
	B	1.309(4)	1.211(4)	1.08	$\theta2$	121.5(3)
	C	1.281(4)	1.226(4)	1.04	$\theta3$	119.6(4)
	D	1.311(4)	1.212(4)	1.08		
	E	1.260(4)	1.249(4)	1.01		
	F	1.315(4)	1.212(4)	1.08		

Table 2. Selected Hydrogen-Bonds between Carboxy (Carboxylato) Groups

	Groups	O···O distance/Å	O–H···O angle/°	Symmetry operation
1	A···F^{i}	2.462(2)	168.3	$-x+1, y-1/2, -y+1$
	B···E^{ii}	2.483(3)	172.5	$x, y-1, z$
	C···D^{iii}	2.538(2)	162.8	$-x, y+1/2, -z+1$
2	B···C^{i}	2.546(2)	174.0	$-x, -y+1, -z$
3	C···D^{i}	2.478(3)	141.3	$-x, -y+1, -z+1$
	A···F^{ii}	2.576(3)	156.2	$-x+1, -y, -z$
4	A···C^{i}	2.511(2)	146.9	$-x+1/2, y, z+1/2$
5	E···F^{i}	2.517(2)	149.1	$-x+1, -y+1, -z+1$
	B···D^{ii}	2.547(2)	162.8	$-x+1, y-1/2, -z+1/2$
	C···F^{ii}	2.676(2)	167.4	$-x+1, y-1/2, -z+1/2$
	D···A^{iii}	2.550(2)	166.9	$x+1, y, z$
6	A1···B1^{i}	2.707(3)	169.6	$-x, -y, -z$
	A1···D2^{i}	2.572(3)	165.0	$-x, -y, -z$
	C1···C2	2.485(3)	179.9	x, y, z
	D1···A2^{ii}	2.526(3)	150.6	$-x, -y+1, -z$
	E1···F1^{iii}	2.597(3)	153.5	$-x+1, -y, -z$
	B2···C2^{ii}	2.593(3)	165.0	$-x, -y+1, -z$
	E2···F2^{iv}	2.567(3)	146.1	$-x-1, -y+1, -z$
7	E···F^{i}	2.619(3)	155.0	$-x+1, -y, -z$
	B···A^{ii}	2.629(3)	163.6	$x, -y+1/2, z+1/2$
	C···E^{ii}	2.509(3)	165.9	$x, -y+1/2, z+1/2$
8	A···B^{i}	2.555(3)	146.2	$-x+1, -y, -z$
	C···C^{ii}	2.449(5)	180.0	$-x, -y, -z$
	E···F^{iii}	2.565(4)	167.9	$-x+1, -y, -z+1$

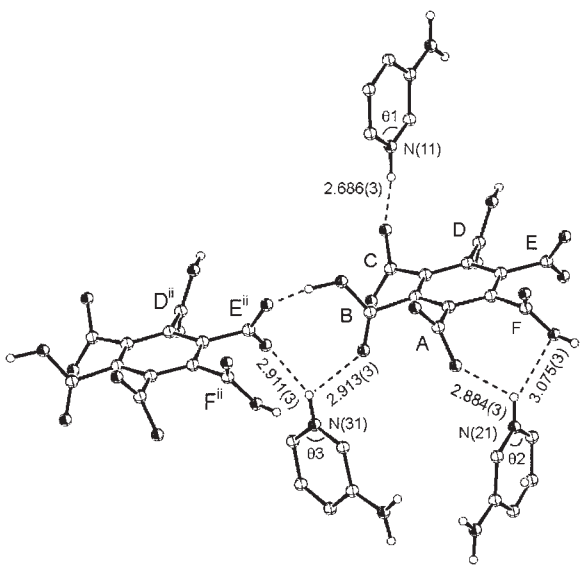


Fig. 4. Hydrogen-bonds between the anion and cation molecules in **1**. N···O distances (Å) in hydrogen-bonds are shown.

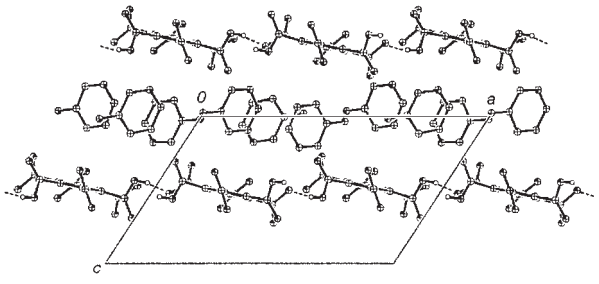


Fig. 5. Side view of the anion sheets and cation layer in **1**. Broken lines represent the hydrogen-bonds between the anions.

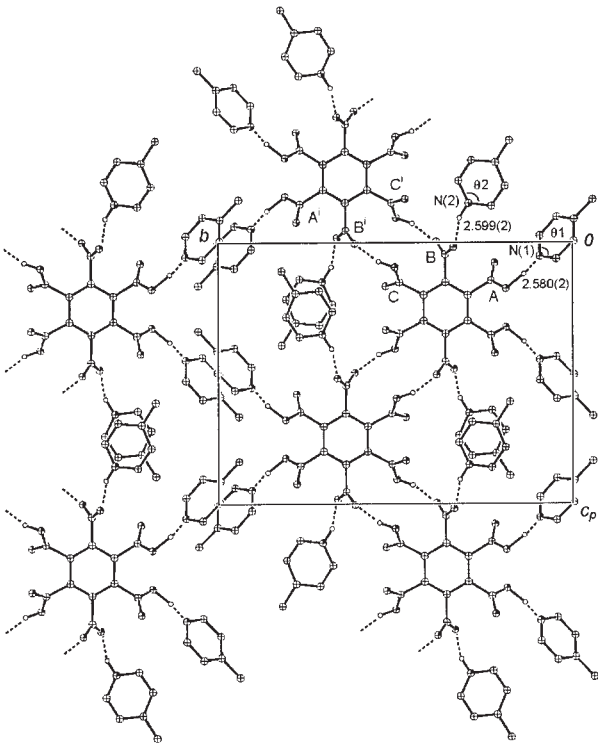


Fig. 6. 1-D belt made up of the anion chain and cations in **2**. N···O distances (Å) in hydrogen-bonds are shown.

D) zig-zag chain along the *c* axis. In this chain, the mellitate anions lie on the same plane. [4-$CH_3C_5H_4NH^+$] and [4-$CH_3C_5H_4N$] are peripherally linked with the anion chain by Type 2 hydrogen-bonds, resulting in the 1-D belt formation along the *c* axis (Fig. 6).

[4-$CH_3C_5H_4NH^+$]$_2$[$C_6(COO)_6H_4^{2-}$]·2CH_3OH ($n = 2$) (3). The geometries of six carboxy (carboxylato) groups (A to F; shown in Fig. 7) in the mellitate anion molecule are summarized in Table 1. None of the *r* values are in the intermediate region (area Ⅲ), so one can assign A and C to carboxylato groups, and B, D, E, and F to carboxy groups. The C–N–C bond angle at N(1) ($\theta1$) indicates that the 4-methylpyridine [N(1)] becomes the pyridinium cation. The angle at N(2) ($\theta2$) is not adequate for the determination of the protonation, since the large thermal vibration (or static disorder) of the molecule is suggested from the largely anisotropic temperature factors. Since the mellitate anion is undoubtedly $n = 2$, it is safe to conclude that the 4-methylpyridine [N(2)] is protonated based

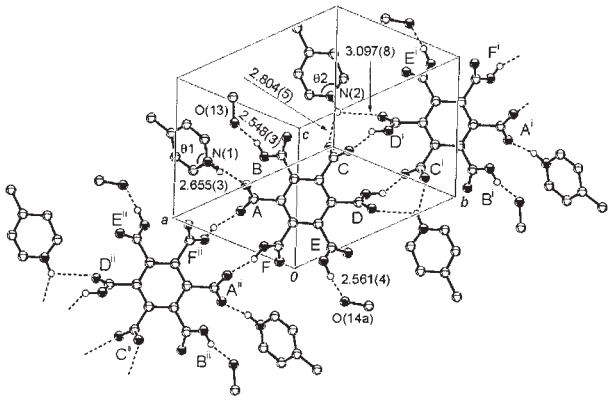


Fig. 7. 1-D belt and the intermolecular hydrogen-bonds in **3**. N···O distances (Å) in hydrogen-bonds are shown.

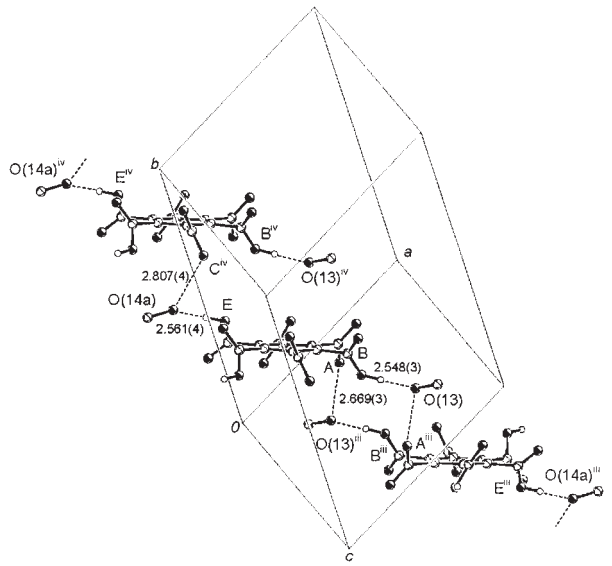


Fig. 8. Hydrogen-bond network via methanol in **3**. iii) $(-x+1, -y, -z+1)$, iv) $(x, y, z-1)$. O···O distances (Å) in hydrogen-bonds are shown.

on the stoichiometry. The compound **3** has two methanol molecules as the crystal solvents, so the formula is [4-$CH_3C_5H_4NH^+$]$_2$[$C_6(COO)_6H_4^{2-}$]·2CH_3OH ($n = 2$).[10]

The neighboring mellitate anions are linked by two pairs of O–H···O hydrogen-bonds (C···D^{i} and D···C^{i}, or A···F^{ii} and F···A^{ii}). Consequently, a 1-D chain is formed along the [−1 1 1] direction (Fig. 7). The Type 2 hydrogen-bonds are formed between [$C_6(COO)_6H_4^{2-}$] and two independent [4-$CH_3C_5H_4NH^+$]'s. These hydrogen-bonds set the cations on both sides of the 1-D anion chain, and make the 1-D belt structure (Fig. 7). The concavities formed in this belt are filled by methanol molecules. The interactions via methanol molecules pile up the 1-D belts along the [1 −1 1] direction (Fig. 8).

[$C_5H_5NH^+$]$_2$[$C_6(COO)_6H_4^{2-}$]·2H_2O ($n = 2$) (4). The mellitate anion lies on a two-fold axis, and the geometries of three independent carboxy (carboxylato) groups (A, B, and C; shown in Fig. 9) are summarized in Table 1. The *r* values and the O···O distances indicate that A and B are carboxy groups, and that C is a carboxylato group. The C–N–C bond angle at N(1) ($\theta1$) shows that the pyridine becomes a pyridinium

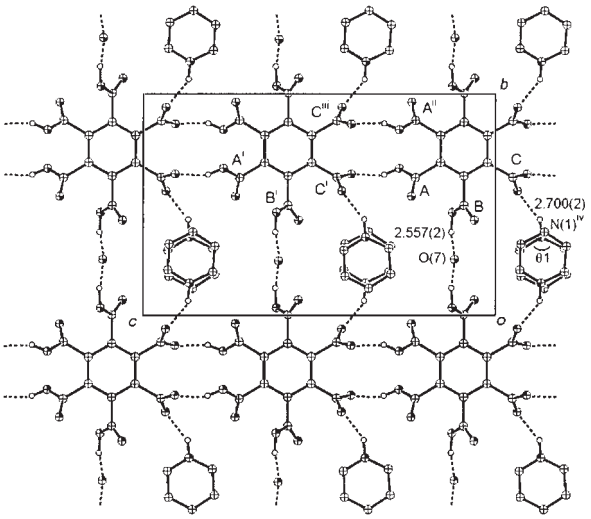


Fig. 9. 1-D belt and the intermolecular hydrogen-bonds in **4**. ii) $(-x+1/2, -y+3/2, z)$, iii) $(x, -y+3/2, z+1/2)$, iv) $(-x, -y+1, -z)$. N···O and O···O distances (Å) in hydrogen-bonds are shown.

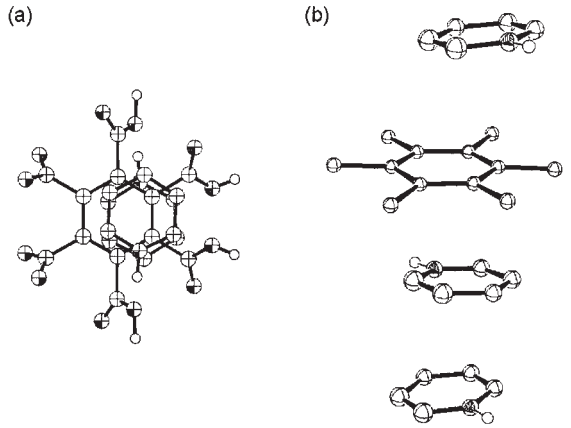


Fig. 10. π-π stacking between the mellitate anion ($n = 2$) and pyridinium in **4**, a) top view, b) side view. The oxygen atoms are omitted for simplicity.

cation. Since the two protons transfer from one mellitate anion and the compound **4** contains two water molecules, the formula is $[C_5H_5NH^+]_2[C_6(COO)_6H_4{}^{2-}]\cdot 2H_2O$ ($n = 2$).

The neighboring anion molecules are linked by two pairs of strong hydrogen-bonds (A···C^{i}, A^{ii}···C^{iii}), forming a 1-D chain along the *c* axis. The pyridinium cations are peripherally linked with the anion chain by a Type 2 hydrogen-bond between C and N(1)^{iv}, forming the 1-D belt structure. Water molecules fill the concavity in the anion belt, and link these belts tightly by the O–H···O hydrogen-bonds (Fig. 9).

Because there are no substituents on the pyridinium molecule, all the cation and anion planes can be almost parallel. The interplaner distances are 3.59 between the cations (Fig. 9), and 3.51 Å between the cation and the mellitate anion in the neighboring belts (Fig. 10). The shortest carbon–carbon interatomic distances are 3.47 and 3.40 Å, respectively. These contacts are shorter than twice the van der Waals radius of carbon,[11] and thus are indicative of π-π interactions.

$[3\text{-}CH_3C_5H_4NH^+]_2[C_6(COO)_6H_4{}^{2-}]$ ($n = 2$) (5). The

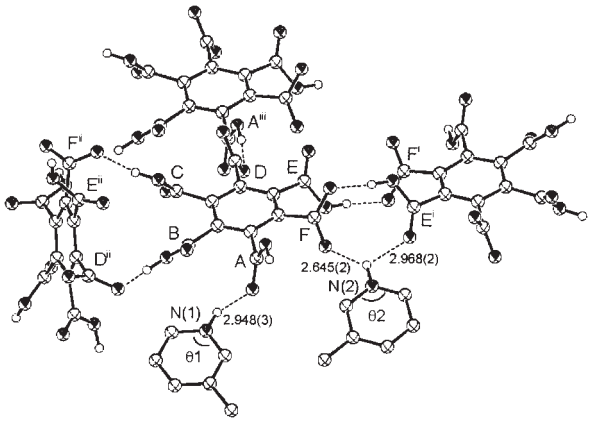


Fig. 11. Intermolecular hydrogen-bonds in **5**. N···O distances (Å) in hydrogen-bonds are shown.

geometries of six independent carboxy (carboxylato) groups (A to F; shown in Fig. 11) in the mellitate anion are summarized in Table 1. From the *r* values, one can clearly assign C and E as carboxy groups and D as a carboxylato group. The values of the other three (A, B, and F) are intermediate, and the assignment has been made as follows. Both A and B are hydrogen-bonding with D (carboxylato), so they must be carboxy groups. Both oxygen atoms in F are hydrogen-bonding with E (carboxy), C (carboxy), and N(2) which is protonated [The C–N–C bond angles at N(1) and N(2) (θ1 and θ2) show that both 3-methylpyridine molecules become the pyridinium cations]. Since the oxygens in F act as a proton acceptor in the hydrogen-bonds and there is no space for F to be a carboxy group, F is assigned as a carboxylato group. This assignment is consistent with the difference Fourier map and with the composition of this salt.

The neighboring mellitate anions are connected by two pairs of hydrogen-bonds (E···F^{i} and F···E^{i}) into an anion dimer, and the dimers are further linked by two pairs of hydrogen-bonds (B···D^{ii} and C···F^{ii}) with other dimers [about 70° of the dihedral angle between the anion molecules at (x, y, z) and at $(-x+1, y-1/2, -z+1/2)$ shown in Fig. 11], forming the 2-D grid structure parallel to the *bc* plane (Fig. 12). The 2-D grids are linked by the D···A^{iii} hydrogen-bonds, forming a channel along the *a* axis. The cation molecules are trapped in this channel by the N–H···O hydrogen-bonds [Type 1 on N(2), and Type 2 on N(1)].

$[3\text{-}CH_3C_5H_4NH^+]_5[C_6(COO)_6H_3{}^{2.5-}]_2\cdot CH_3OH$ ($n =$ 2.5) (6). There are two independent mellitate anions (I, II), and the geometries of independent carboxy (carboxylato) groups (A1 to F1 and A2 to F2; shown in Fig. 13) are summarized in Table 1. The *r* values and their O···O distances in hydrogen-bonds indicate that A1, F1 and F2 are carboxylato groups, and that B1, D1, E1, B2, D2, and E2 are carboxy groups. Since the C1···C2 pair has intermediate *r* values and the short O···O hydrogen-bonding distance [area III in Fig. 1(b)], one proton is shared equally by them. The *r* value of A2 and the O···O distance in the hydrogen-bond do not clearly correspond to the areas shown in Fig. 2(b). However, A2 can be assigned as a carboxylato group, since the counterpart of the hydrogen-bond (D1) is a carboxy group, and there is no electron density indicative of the existence of *syn*-hydrogen in the

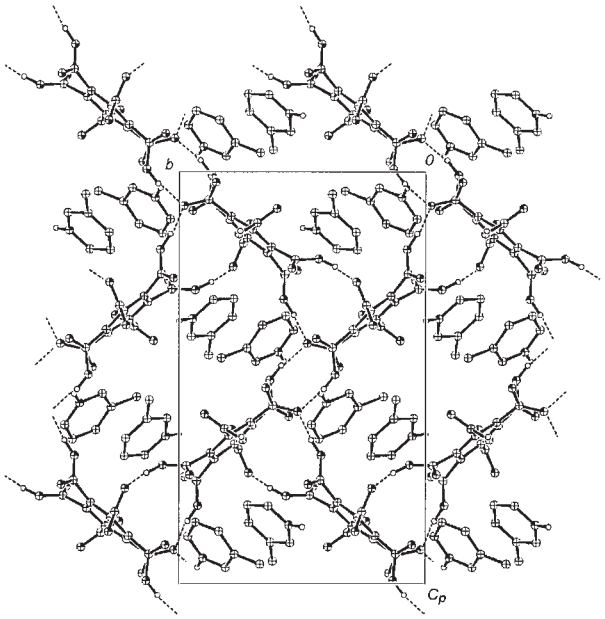


Fig. 12. 2-D channel connected by hydrogen-bonds between the anions in **5**.

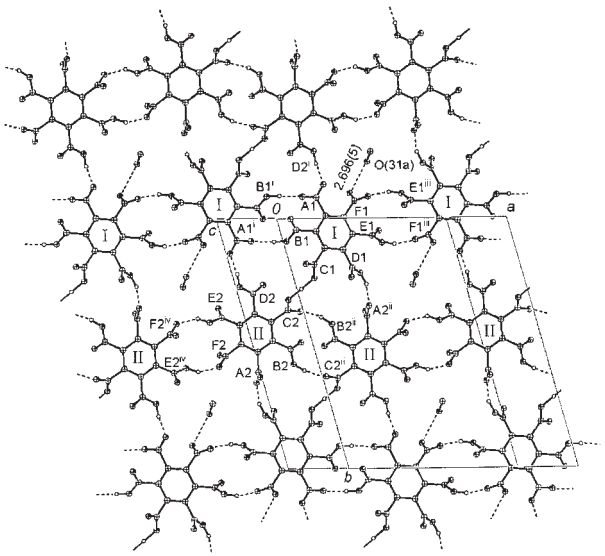


Fig. 13. 2-D sheet of the anions (I and II) with methanol molecules in **6**.

difference Fourier map around it. The temperature factors of the molecules at N(2) (θ2) and N(3) (θ3) are very large, so a full discussion about the C–N–C angles is rather difficult. However, one can assign that the crystallographically independent five 3-methylpyridine molecules become the 3-methylpyridinium cations[12] not only from the C–N–C bond angles of the pyridine rings, but also from the fact that the sum of the negative charge of two independent anion molecules is 5. The assignment is consistent with the difference Fourier maps around the pyridine rings. Since compound **6** has one methanol molecule as the crystal solvent, the formula is [3-$CH_3C_5H_4NH^+$]$_5$[C_6(COO)$_6H_{3.5}^{2.5-}$]$_2$·CH_3OH ($n = 2.5$).[13]

Two sets of four pairs of hydrogen-bonds (A1···B1^{i}, B1···A1^{i}, E1···F1^{iii}, and F1···E1^{iii} for anion I, and B2···C2^{ii}, C2···B2^{ii}, E2···F2^{iv}, and F2···E2^{iv} for anion II) link the anion molecules into two 1-D chains along the *a* axis, and further hydrogen-bonds (A1···D2^{i}, C1···C2, and D1···A2^{ii}) make them into a 2-D sheet. A methanol molecule compensates the space in the sheet.

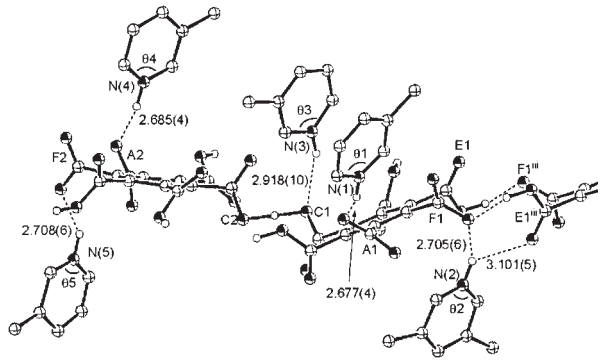


Fig. 14. Intermolecular hydrogen-bonds between the anions and cations in **5**. N···O distances (Å) in hydrogen-bonds are shown.

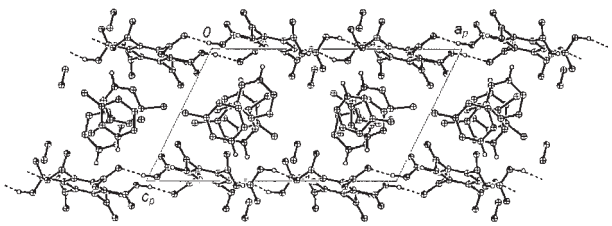


Fig. 15. Side view of the anion sheets and cation layer in **6**.

N(2) of 3-methylpyridinium cation forms a Type 1 hydrogen-bond with F1 and E1^{iii}. N(1), N(3), N(4), and N(5) form Type 2 hydrogen-bonds with A1, C1, A2, and F2, respectively (Fig. 14). Since an additional interaction, N(5)···A2, exists, the mode of hydrogen-bond on N(5) may partly have a Type 1 character. These N–H···O hydrogen-bonds insert the cations between the 2-D anion sheets (Fig. 15). The cations form the columnar structure with nearly parallel stacking, and the molecular planes are almost perpendicular to the anion sheet.

[$C_9H_7NH^+$]$_2$[C_6(COO)$_6H_4^{2-}$]·CH_3OH ($n = 2$) (7). The geometries of six independent carboxy (carboxylato) groups (A to F; shown in Fig. 16) in the mellitate anion are summarized in Table 1. The *r* values clearly indicate that E is a carboxylato group, and that B, C, D, and F are carboxy groups. Applying the relation between the C–N–C bond angle and the hydrogen position on the pyridine ring, the corresponding bond angles of the quinoline ring (θ1 and θ2) indicate that both isoquinoline molecules become the cations. Though the *r* value of A is in the intermediate region, it can be assigned as a carboxylato group based on the stoichiometry and relatively long O···O distance in the A···B pair. These hydrogen positions are also consistent with the difference Fourier maps around N(1) and N(2). Since methanol is contained as the crystal solvent, the formula of the compound **7** is [$C_9H_7NH^+$]$_2$-[C_6(COO)$_6H_4^{2-}$]·CH_3OH ($n = 2$).

Two pairs of the O–H···O hydrogen-bonds [E···F^{i} and F···E^{i} in Fig. 16(a)] link the neighboring mellitate anions, [C_6(COO)$_6H_4^{2-}$], into an anion dimer, and two further pairs

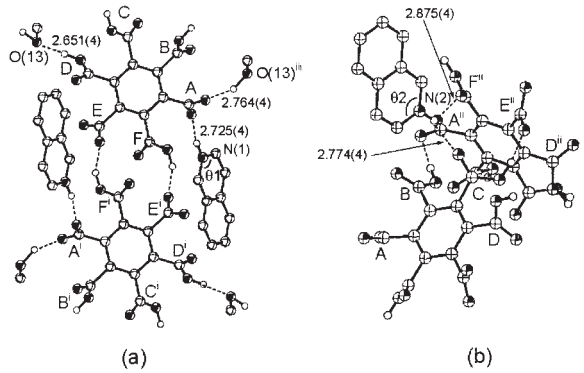


Fig. 16. Two kinds of the hydrogen-bond patterns between the anions in **7**; a) in the co-planar dimer unit, b) between the dimer units. The symmetry operation (iii) is $(x+1, -y+1/2, z+1/2)$. N···O distances (Å) in hydrogen-bonds are shown.

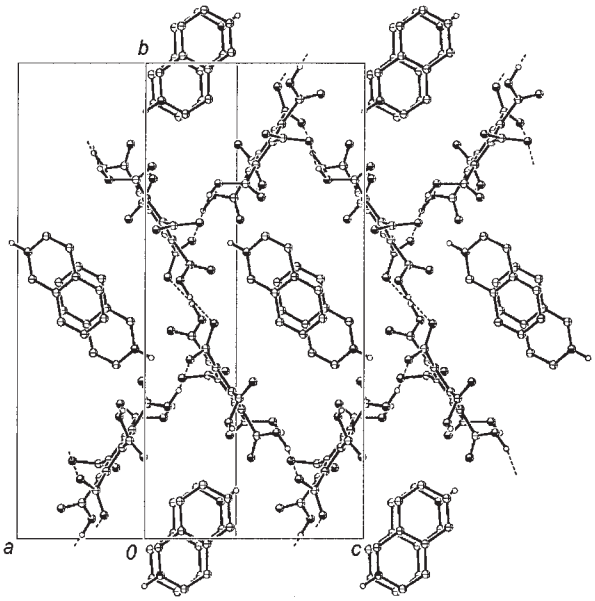


Fig. 17. 2-D channel of the anions and the cation columns in **7**.

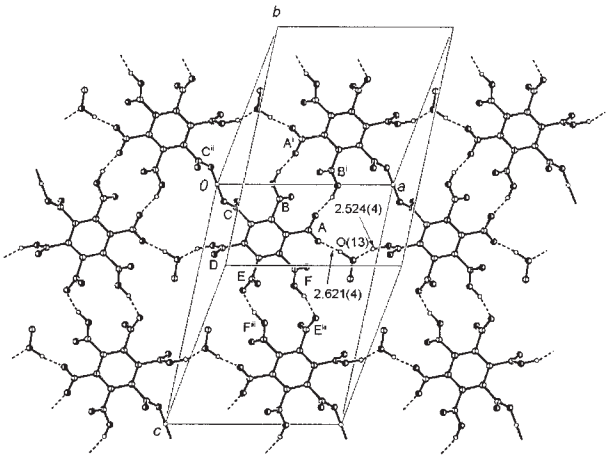


Fig. 18. 2-D sheet of the mellitate anions ($n = 2.5$) with methanol molecules in **8**. O···O distances (Å) in hydrogen-bonds are shown.

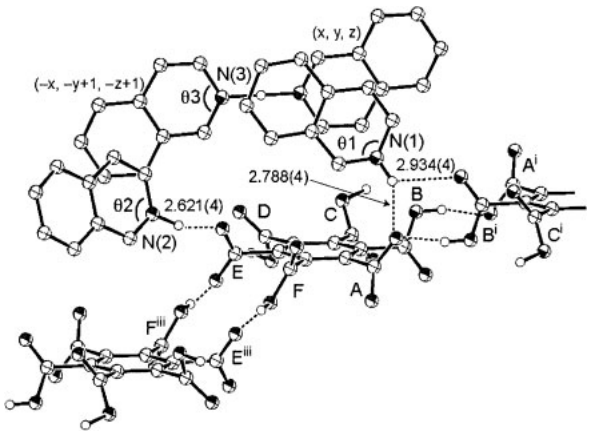


Fig. 19. Hydrogen-bonds between the mellitate anions and between the anion and isoquinolinium in **8**. Note that the isoquinoline with N(3) shares one proton with the other isoquinoline related by the inversion symmetry. N···O distances (Å) in hydrogen-bonds are shown.

of hydrogen-bonds [B···A^{ii} and C···E^{ii} in Fig. 16(b)] link the anion dimers with the neighboring other dimers (about 70° of dihedral angle) into a 2-D grid (Fig. 17). The 2-D grids are connected by the O–H···O hydrogen-bonds via methanol molecules to form the channel structures along the [1 0 1] direction. The isoquinolinium cations are trapped in the channel by the N–H···O hydrogen-bonds [Type 1 on N(2), Type 2 on N(1)], and form the columnar structure. The angle between the grid layer and the cation column is about 60°.

$[C_9H_7NH^+]_2[C_9H_7NH_{0.5}{}^{0.5+}][C_6(COO)_6H_{3.5}{}^{2.5-}]\cdot CH_3OH$ ($n = 2.5$) (8). The geometries of six independent carboxy (carboxylato) groups (A to F; shown in Fig. 18) in the mellitate anion are summarized in Table 1. The *r* values and their O···O distances in hydrogen-bonds clearly indicate that A and E are carboxylato groups, and B, D, and F are carboxy groups. From the *r* value and the O···O hydrogen-bond distance, C is found to be situated in the area Ⅲ [Fig. 1(b)]. One proton is thus equally shared by the two –COO groups (C and C^{ii}). The C–N–C bond angles at N(1) and N(2) ($\theta1$ and $\theta2$) indicate that both isoquinoline molecules become isoquinolinium cations. As for N(3), the situation is slightly different. The shortest intermolecular contact is N(3)···N(3) pair related by the inversion center. The distance is extremely short, 2.659(7) Å. This clearly indicates that a strong hydrogen-bond exists between N(3) at (x, y, z) and that at $(-x, 1-y, 1-z)$. Indeed, $\theta3$ is in the intermediate region in Fig. 2, and two isoquinoline molecules equally share one proton. Methanol is contained as the crystal solvent, so the formula of the compound **8** is $[C_9H_7NH^+]_2[C_9H_7NH_{0.5}{}^{0.5+}][C_6(COO)_6H_{3.5}{}^{2.5-}]\cdot CH_3OH$ ($n = 2.5$).

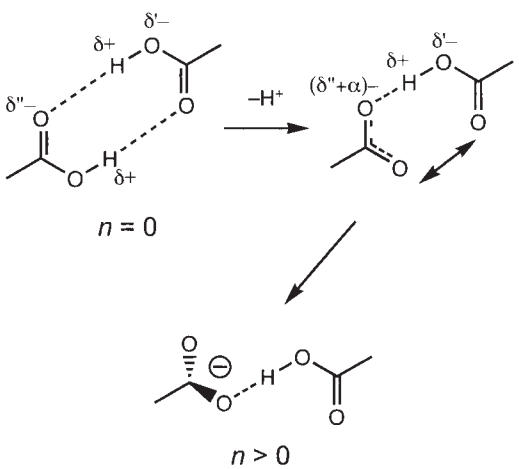
The neighboring mellitate anions, $[C_6(COO)_6H_{3.5}{}^{2.5-}]$, are linked by the O–H···O hydrogen-bonds between the carboxy and carboxylato groups (A···B^{i}, C···C^{ii}, and E···F^{iii}) and via methanol molecules [A···O(13) and D···O(13)] to form a 2-D anion sheet in the *ac* plane (Fig. 18).

Through the Type 1 [N(1)] and Type 2 [N(2)] hydrogen-bonds (Fig. 19), the isoquinolinium molecules are inserted between the anion sheets, and their molecular planes are almost

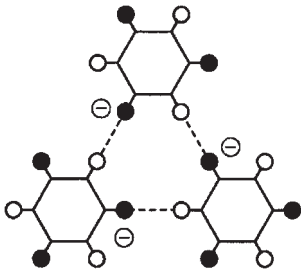
perpendicular to the sheet. The hydrogen-bonded isoquinolinium pair is also arranged in the same cation layer, and no hydrogen-bonds are formed with the mellitate anion.

Discussion

Neutral mellitic acid forms a 2-D sheet resulting from the hydrogen-bonds spreading out to six directions.[6] The hydrogen-bonds are "paired hydrogen-bonds," and the O···O distances are about ~2.65 Å. However, when the deprotonation occurred, a "paired hydrogen-bond" has never been seen. This may be due to the following reason. When a mellitic acid is partly deprotonated, each mellitate anion possesses both –COOH and $–COO^-$ groups. The –COOH group may form a hydrogen-bond with either –COOH and $–COO^-$ groups. However, the bond with the latter is preferable due to the additional Coulombic attraction compared with the hydrogen-bond between C–OH and C=O (Scheme 3). The hydrogen-bond distance would be shorter than the "paired hydrogen-bond" due to the attractive force between the carboxy and carboxylato groups. In order to avoid unreasonable O···O atomic contacts, a carboxylato group is turned around the O–H···O hydrogen-bond, and a stronger "single hydrogen-bond" (O···O; <2.6 Å) is formed (Scheme 3). On the other hand, the hydrogen-bond may also be strong in the combination of carboxylic acid and pyridine derivatives.[14] In fact, the formation of the supramolecular architecture based on this interaction is widely studied and is very useful for crystal engineering.[15] However, in the salts of pyromellitate anions with pyridiniums, the formation of infinite networks by the "single hydrogen-bonds" precedes the interruption by pyridiniums,[16] when the carboxy (carboxylato) groups are available for the formation of intermolecular hydrogen-bonds (not participating in the intramolecular hydrogen-bonds). Since no breakdown of the network between mellitate anions ($n = 3$, 2, and 2.5) has been observed, the "single hydrogen-bond" is considered to be much stronger and precedes the interaction of carboxylic acid (carboxylate) ··· pyridine (pyridinium). The pyridine (pyridinium) molecules are always linked at the periphery of the anion network by Type 1 or 2 hydrogen-bonds. Since there are no "paired hydrogen-bonds" in the crystals studied, the carboxylic acid (carboxylate) ··· pyridine (pyridinium) interaction may be stronger than that.



Scheme 3.

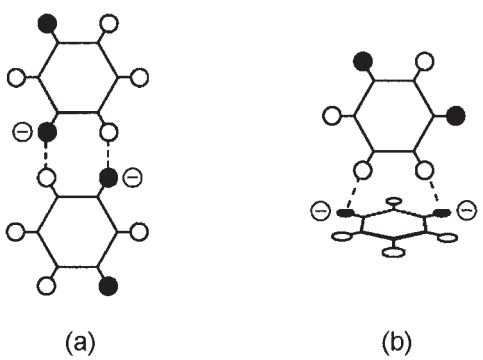


Scheme 4.

In the case where three protons are dissociated ($n = 3$), all the "paired hydrogen-bonds" in the neutral mellitic acid crystal can be displaced by "single hydrogen-bonds," and the anions form a 2-D sheet. Since the self-organizing property is strong, the repetition of the hydrogen-bonding unit shown in Scheme 4 leads to the formation of the 2-D sheet structure. It is worth noting that any deprotonation pattern of mellitate anion with $n = 3$, namely, 1, 2, 3-, 1, 2, 4-, or 1, 3, 5-carboxylato groups, can maintain the 2-D sheet structure.

On the other hand, the mellitate anions with $n = 2$ does not form a 2-D sheet. Instead, the "dual hydrogen-bond," neighboring anions are bound by two carboxy–carboxylato pairs of the "single hydrogen-bonds" [Scheme 5(a)], appears to be the dominant hydrogen-bond unit. This type of hydrogen-bond has been seen in the salt of tetrachlorophthalate with 2-methyl-5-ethylpyridinium, where the anions form a dimer.[17] In the salts with $n = 2$, the repetition of this "dual hydrogen-bond" unit often makes a 1-D anion chain. In the compound **2**, a zig-zag chain is formed, while in **3** and **4**, the mellitate anions form a straight chain. In addition to the parallel "dual hydrogen-bond" [Scheme 5(a)], the standing "dual hydrogen-bond" is found in **5** and **7** [Scheme 5(b)]. The hydrogen-bond in Scheme 5(b) has never been seen in the crystals of an aromatic carboxylic acid. The 2-D grid structure in both compounds is composed of the co-planar dimers [consistent with Scheme 5(a)], and the standing "dual hydrogen-bond" [Scheme 5(b)] between the dimers. These two types of "dual hydrogen-bond" units [Scheme 5(a), (b)] are dominant in the mellitate anion salts with $n = 2$, and show their strong self-organizing ability.

In **6**, the crystallographically independent anions (I and II) form two kinds of independent 1-D chains along the *a* axis. In **8**, the anions form a zig-zag chain along the *c* axis. These 1-D chains constructed by the co-planar "dual hydrogen-bonds"



Scheme 5.

Table 3. Crystal Data and Structure Refinement Parameters

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{27}H_{24}N_6O_{12}$	$C_{36}H_{34}N_4O_{12}$	$C_{26}H_{28}N_2O_{14}$	$C_{22}H_{20}N_2O_{14}$	$C_{24}H_{20}N_2O_{12}$	$C_{55}H_{51}N_5O_{25}$	$C_{31}H_{24}N_2O_{13}$	$C_{40}H_{31}N_3O_{13}$
Formula Weight	624.52	714.68	592.51	536.41	528.43	1182.03	632.54	761.70
Crystal System	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	triclinic	monoclinic	triclinic
Space Group	$P2_1$	$C2/c$	$P\bar{1}$	$Pccn$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	16.556(1)	12.378(1)	10.462(1)	10.785(1)	9.763(1)	17.052(1)	12.231(2)	11.578(1)
b/Å	9.530(1)	19.400(1)	14.525(1)	11.365(1)	11.829(1)	19.153(1)	22.486(2)	14.383(1)
c/Å	9.989(1)	14.177(1)	9.641(1)	18.228(1)	19.510(1)	10.021(5)	10.678(2)	15.929(1)
α/°	—	—	102.77(1)	—	—	92.86(1)	—	137.0(1)
β/°	123.41(1)	93.26(1)	103.77(1)	—	93.30(1)	116.49(1)	109.48 (1)	102.21(1)
γ/°	—	—	77.39(1)	—	—	74.32(1)	—	74.11 (1)
V/Å^3	1315.54(8)	3398.9(2)	1366.4(4)	2234.1(3)	2249.4(2)	2810.9(2)	2768.7(6)	1739.8(1)
Z	2	4	2	4	4	2	4	2
D_x/g cm^{-3}	1.576	1.397	1.440	1.595	1.560	1.396	1.517	1.454
μ(Mo-Kα)/cm^{-1}	1.26	1.06	1.18	1.36	1.27	1.12	1.20	1.10
$2\theta_{max}$	55.0	54.9	54.8	54.8	55.0	55.0	55.0	55.0
Temp. of data collection /K	113	123	103	103	100	131	103	123
No. of unique reflections	3186	3863	6107	2874	5146	12788	6332	7872
R_{int}	0.021	0.033	0.032	0.040	0.030	0.030	0.045	0.038
No. of observations $[I > 1.5\sigma(I)]$	3008	3030	4770	2114	4230	8778	4129	4529
No. of Variables	413	238	394	175	349	795	421	512
R; R_w	0.036; 0.045	0.055; 0.062	0.082; 0.102	0.058; 0.074	0.048; 0.057	0.081; 0.096	0.069; 0.071	0.074; 0.067
Goodness of fit indicator	1.52	1.74	2.53	1.84	1.65	1.91	1.36	1.25

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2\}^{1/2}$.

show that the anion ($n = 2.5$) also has the $n = 2$ character. In addition, the chains are linked into a 2-D sheet by strong hydrogen-bonds mediated by the protons equally shared between the two –COO groups. The large space in the 2-D sheet is filled by methanol molecules. These structural features are the dominant character of the anions with $n = 2.5$.

The pattern of the molecular arrangements varied by n (Scheme 4 and 5) is reflected in the symmetry of the crystals. When $n = 3$ (Scheme 4), it is not possible for this pattern to accommodate any symmetry centers in the sheet. As a result, **1** ($n = 3$) has an acentric space group, and the other crystals have centric space groups.

In these salts, five salts contain the solvent molecules of methanol or water contained in methanol or in air. Although in the crystals of several 5-alkoxyisophthalic acids, the pattern of hydrogen-bond depends on the solvate molecules,[2] the present salts can not be grown from the other solvents. When the crystallization occurs, the formation of the hydrogen-bonds between the mellitate anion molecules may precede, and there may be several stable anion arrangements (for example, two types of "dual hydrogen-bonds"). Certainly, the inclusion of methanol or water molecules is thought to be necessary to keep one of the anion arrangements in the crystalline state, yet the strong self-organizing ability of the mellitate anions is considered as a key factor for the growth of the present crystals.

Conclusion

The mellitate anions have various molecular arrangements depending on the deprotonation number, n. They are linked by "single hydrogen-bonds," and show strong self-organizing ability. An anion with $n = 3$ forms a "triangular hydrogen-bond" unit (Scheme 3) to form a 2-D sheet. The anion with $n = 2$ can form two types of the "dual hydrogen-bond" units [Scheme 4(a) and (b)], composed of two "single hydrogen-bond"s. A 1-D chain or a 2-D grid may be formed by these hydrogen-bond units. In the crystals of the anion with $n = 2.5$, a 1-D chain is formed, and then the existence of the half shared proton leads to the 2-D sheet structure.

The chain, sheet and grid of the mellitate anion assemblies can be used to arrange the counter cation molecules in the defined space, and to control the physical properties (electrical conductivity, magnetism, and so on) based on the cation arrangements.

Experimental

Preparation of Materials. Mellitic acid and a large excess amount of bases (typical molar ratio is 1:10) were separately dissolved in methanol, and then these solutions were mixed at room temperature. The solutions were subjected to slow evaporation of the solvent at room temperature in air or in a nitrogen gas flow. After one or a few days, colorless block-shaped single crystals appeared. To check the presence of two or more different crystalline forms, X-ray diffraction measurements were performed for several crystals in the same batch. Consequently, in the cases of 4-methylpyridine and isoquinoline, it was revealed that the solvated and unsolvated crystals with the same pyridine derivative were grown in the same batch. They have practically identical appearances (compound **2** and **3**, **7** and **8**). In the case of 3-methylpyridine, compound **5** was grown during two days after the beginning of the evaporation, and the further evaporation of that solution sometimes allows us to obtain compound **6**.

X-ray Structure Determination. Diffraction data for all the samples were recorded on a Rigaku R-AXIS Rapid imaging plate diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). The temperature was regulated by a cold nitrogen gas flow instrument. The crystal data are summarized in Table 3. The structures were solved by direct methods (SIR-92[18]) and refined with the data [$I > 1.5\sigma(I)$] on F using the teXsan program package.[19]

The hydrogen positions in the O–H···O and O–H···N (O···H–N) hydrogen-bonds were determined by applying the geometric features mentioned in the Results section to both proton donor and proton acceptor in each hydrogen-bond, while checking the consistency with the electron densities. Their thermal parameters were refined as isotropic. The other hydrogen atoms were fixed at each ideal position.

In the analysis of **1** (with an acentric space group, $P2_1$), the Bijvoet pairs were averaged, and the anomalous dispersion effects were included in the F calculation.

CCDC-208167 (**1**), CCDC-208168 (**2**), CCDC-208169 (**3**), CCDC-208170 (**4**), CCDC-208171 (**5**), CCDC-208172 (**6**), CCDC-208173 (**7**), and CCDC-208174 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; or e-mail: deposit@ccdc.cam.uk).

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

References

1 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, **34**, 2311 (1995).

2 "Design of Organic Solids (Topics in Current Chemistry, Vol. 198)," ed by E. Weber, Springer (1998).

3 D. J. Duchamp and R. E. Marsh, *Acta Crystallogr., Sect. B*, **25**, 5 (1969).

4 a) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, **101**, 1629 (2001). b) S. V. Kolotuchin, P. A. Thiessen, E. E. Fenlon, S. R. Wilson, C. J. Loweth, and S. C. Zimmerman, *Chem. Eur. J.*, **5**, 2537 (1999).

5 A. J. Lough, P. S. Wheatley, G. Ferguson, and C. Glidewell, *Acta Crystallogr., Sect. B*, **56**, 261 (2000).

6 S. F. Darlow, *Acta Crystallogr.*, **14**, 159 (1961).

7 a) Mn(II) ($n = 6$); L. P. Wu, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, J. Fukui, and M. Munakata, *Inorg. Chim. Acta*, **239**, 165 (1995). b) Co(II) ($n = 6$); C. Robl and S. Hentschel, *Z. Naturforsch., Teil B*, **46**, 1188 (1991). c) Y(III) ($n = 6$); C. Robl and S. Hentschel, *Z. Naturforsch., Teil B*, **47**, 1561 (1992). d) Al(III) ($n = 6$); C. Robl and W. F. Kuhs, *J. Solid State Chem.*, **92**, 101 (1991). e) Ce(III) ($n = 6$), Eu(III) ($n = 6$), Yb(III) ($n = 6$); L. P. Wu, M. Munakata, T. Kuroda-Sowa, M. Maekawa, and Y. Suenaga, *Inorg. Chim. Acta*, **249**, 183 (1996). f) Np_2O_4 ($n = 6$); F. Nectoux, H. Abazli, J. Jove, A. Cousson, M. Pages, and M. Gasperin, *J. Less-Common Met.*, **97**, 1 (1984). g) Ni(II) ($n = 4$); H. Endres and A. Knieszner, *Acta Crystallogr., Sect. C*, **40**, 770 (1984). h) K ($n = 6$), Cs ($n = 5$); J. A. Harnisch, L. M. Thomas, I. A. Guzei, and R. J. Angelici, *Inorg. Chim. Acta*, **286**, 207 (1999). i) Ca ($n = 4$); V. A. Uchtman and R. J. Jandacek,

Inorg. Chem., **19**, 350 (1980). j) Cu(II) ($n = 5$); H. Tamura, K. Ogawa, and W. Mori, *J. Crystallogr. Spectrosc. Res.*, **19**, 203 (1989).

8 Crystal information was obtained from the Cambridge Structural Database (CSD: F. H. Allen, O. Kennard, *Chem. Des. Autom. News*, **8**, 1 (1993)), update ver. 5.23 (April 2002) with 257162 entries. The data of crystals published after 1975 were used in Fig. 1. The intramolecular hydrogen-bonds were excluded, because the extra geometrical stress may influence the hydrogen-bond structure.

9 T. Steiner, *Angew. Chem., Int. Ed.*, **41**, 48 (2002).

10 Methanol molecule is orientationally disordered and the ratio of the occupancy of O(14) is O(14a):O(14b) = 0.83:0.17 [O(14b) is omitted in Fig. 7].

11 "Molecular Crystals and Molecules," A. I. Kitaigorodsky, Academic Press (1973).

12 The methyl group in 3-methylpyridinium [N(2)] is disordered at 3- and 5-positions, and their occupancies are both 0.5.

13 The oxygen atom of methanol molecule is orientationally disordered, and the ratio of the occupancy is O(31a):O(31b) = 0.665:0.335 [O(31b) is omitted in Fig. 13].

14 C. B. Aakeroy and A. M. Beatty, *Aust. J. Chem.*, **54**, 409 (2001).

15 a) N. Shan, A. D. Bond, and W. Jones, *Cryst. Eng.*, **5**, 9 (2002). b) M. Tomura and Y. Yamashita, *Chem. Lett.*, **2001**, 532.

16 K. Biradha and M. J. Zaworotko, *Cryst. Eng.*, **1**, 67 (1998).

17 J. Galloy, J.-P. Putzeys, G. Germain, and M. V. Meerssche, *Acta Crystallogr., Sect. B*, **32**, 2718 (1976).

18 A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, and G. Polidori, *J. Appl. Crystallogr.*, **27**, 435 (1994).

19 Crystal Structure Analysis Package, Molecular Structure Corporation, 3200 Reserch Forest Drive, The Woodlands, TX 77381 (1985 and 1999).