July, 1989] © 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 2189—2195 (1989) 2189

Molecular Recognition in the Formation of Conglomerate Crystal. 2. The Role of Arenesulfonic Acid in the Conglomerate Crystals of Amino Acid Salts

Hiroki KIMOTO, Kazuhiko SAIGO,* Yuji OHASHI,† and Masaki HASEGAWA
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
†Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112

(Received December 9, 1988)

The structures of conglomerate crystals, *p*-chlorobenzenesulfonic acid salt of L-alanine, *p*-toluenesulfonic acid salt of L-serine, and benzenesulfonic acid salt of L-leucine, were determined by X-ray analysis. The crystals are built up of repeating units consisting of two amine components and two acid components to form a helical column by hydrogen bonds. The arrangements of the arenesulfonic acids are found to be similar to each other in these systems. Moreover, the arrangements have similarity to those of cinnamic acid in the crystals of cinnamic acid salts of (*R*)-1-phenylethylamine and of (*R*)-1-(4-isopropylphenyl)ethylamine, which are also conglomerates. These results suggest that our proposed criteria for the choice of an achiral derivatizing agent in the transformation of a racemic compound into a conglomerate crystal is appropriate.

The diastereomeric salt method is the most popular in the optical resolution. But, in the resolution, a stoichiometric amount of an optically pure compound is usually required as a resolving agent, and it is difficult to get both enantiomers from a racemic modification by a simple operation.[1] Although this difficulty can be solved by the preferential crystallization method, this method is applicable to only uncommon conglomerate crystals. They are ascertained by trial-and-error procedure using an achiral derivatizing agent.[1] Then, it is worthy to find the criteria for the choice of an achiral compound in the transformation of a racemic compound into a conglomerate crystal. In the previous paper,[2] we reported the structures of two conglomerate crystals, cinnamic acid salts of α-substituted benzylamine derivatives, and proposed the criteria on the structural requirement for an achiral acid in the transformation of a racemic amine into a conglomerate crystal.

On the other hand, it is already known that the arenesulfonic acid salts of some amino acids are also conglomerate crystals.[3–6] We report here the crystal structures of three conglomerate crystals, *p*-toluenesulfonic acid salt of L-serine (**1**), *p*-chlorobenzenesulfonic acid salt of L-alanine (**2**), and benzenesulfonic acid salt of L-leucine (**3**) to verify our hypotheses for the transformation.

Experimental

Crystal Structure Determination. Colorless plate-like crystals, **1**, **2**, and **3** were grown from saturated aqueous solutions of equimolar mixtures of the amino acids and the arenesulfonic acids, respectively. The specimen used was a fragment of a plate. The space group was determined by

Table 1. Crystal Data and Details of Refinement

	1	**2**	**3**
Formula	$C_3H_7NO_3\cdot C_7H_8O_3S$	$C_3H_7NO_2\cdot ClC_6H_5O_3S$	$C_6H_{13}NO_2\cdot C_6H_6O_3S\cdot H_2O$
M	276.8	281.3	306.9
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	6.853(0)	8.806(1)	9.921(1)
b/Å	27.306(2)	26.528(9)	25.741(2)
c/Å	6.783(0)	5.247(0)	6.216(0)
V/Å^3	1269.3(2)	1225.7(2)	1587.4(2)
Z	4	4	4
D_m/g cm^{-3}	1.45	1.50	1.30
D_c/g cm^{-3}	1.449	1.525	1.285
μ(Cu $K\alpha$)/cm^{-1}	23.46	43.03	19.15
Crystal size/mm^3	0.45×0.40×0.30	0.30×0.30×0.40	0.45×0.45×0.30
No. of unique reflections	1235	1176	1505
No. of observed reflections	1199	1142	1477
No. of parameters	205	190	244
$\Delta\rho_{max}$/e Å^{-3}	+0.37	+0.93	+0.26
$\Delta\rho_{min}$/e Å^{-3}	−0.71	−0.56	−0.65
$(\Delta/\rho)_{max}$	0.226	0.109	0.017
R	0.069	0.059	0.064
R_w	0.072	0.061	0.069

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters for **1**

Atom	*x*	*y*	*z*	B_{eq}[11]/Å^2
S(1)	9370(2)	3978(0)	2261(2)	2.4(0)
C(1)	5253(8)	4339(2)	−2366(8)	2.4(1)
O(1)	4740(7)	4853(2)	512(6)	3.3(1)
O(2)	8554(7)	3961(2)	4241(7)	3.8(1)
N(1)	7147(6)	4600(2)	−2595(7)	2.5(1)
O(3)	9077(7)	4443(1)	1253(6)	3.6(1)
C(2)	4373(8)	4255(2)	−4383(8)	2.7(1)
O(4)	11421(6)	3834(2)	2207(7)	3.9(1)
O(5)	4747(7)	4515(2)	−5744(6)	3.5(1)
C(3)	4866(18)	2626(3)	−3137(15)	6.4(3)
C(4)	6271(9)	3378(2)	1393(10)	3.5(1)
C(5)	3854(8)	4656(2)	−1150(8)	2.9(1)
C(6)	8121(7)	3551(2)	833(8)	2.4(1)
O(6)	3171(8)	3888(2)	−4386(8)	2.4(1)
C(7)	7808(11)	3104(2)	−2232(10)	4.2(2)
C(8)	5270(10)	3069(2)	123(13)	4.2(2)
C(9)	5992(11)	2941(2)	−1696(10)	3.9(2)
C(10)	8909(9)	3410(2)	−985(9)	3.2(1)

Table 3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters for **2**

Atom	*x*	*y*	*z*	B_{eq}[11]/Å^2
S (1)	4468(1)	8227(0)	326(2)	2.6(0)
Cl(1)	5771(4)	10380(1)	−4030(5)	8.0(1)
O (1)	3181(4)	8280(1)	2033(8)	3.6(1)
O (2)	5870(4)	8102(1)	1702(8)	3.3(1)
O (3)	4184(4)	7897(1)	−1798(8)	3.8(1)
C (1)	5610(5)	6830(2)	2803(10)	2.8(1)
O (4)	3713(4)	6731(1)	−303(8)	3.6(1)
N (1)	5960(4)	7196(1)	4869(9)	2.9(1)
C (2)	4147(8)	9255(2)	221(14)	4.7(2)
C (3)	5980(8)	9368(2)	−3998(13)	4.6(2)
O (5)	3064(4)	7103(1)	3365(8)	3.6(1)
C (4)	4805(5)	8839(2)	−940(10)	2.9(1)
C (5)	5359(9)	9778(2)	−2839(14)	5.0(2)
C (6)	5838(9)	6296(2)	3753(17)	5.5(2)
C (7)	5701(6)	8896(2)	−3060(11)	3.7(1)
C (8)	4407(11)	9731(2)	−752(15)	5.7(2)
C (9)	3996(5)	6914(2)	1977(11)	2.6(1)

photographs. Data were collected up to 2θ=125° on a Rigaku four-circle diffractometer using graphite-monochromated Cu $K\alpha$ (1.5418 Å) radiation by ω–2θ scan. Standard reflections showed no significant intensity change. Of unique reflections measured, those as observed with $|F_o|>3\sigma(|F_o|)$ were used. The intensities were corrected for Lorentz, polarization, but not for absorption nor extinction. The structure was solved by the direct method (MULTAN 78[7]) and was refined by the full-matrix least-squares (SHELX 76[8]). Crystal data and details of refinement are summarized in Table 1. Scattering factors were taken from "International Tables for X-ray Crystallography".[9] Computations were performed on Hitachi M-680H and M-682H in the Computer Centre of the University of Tokyo.

Results and Discussion

Fractional coordinates for the crystals of **1**, **2**, and **3** are given in Tables 2, 3, and 4, respectively.[10] Labeled

Table 4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters for **3**

Atom	*x*	*y*	*z*	B_{eq}[11]/Å^2
S(1)	8214(1)	3511(0)	4327(2)	3.8(0)
O(1)	8083(5)	3519(1)	6619(7)	7.1(1)
O(2)	9292(3)	3170(1)	3580(4)	4.3(1)
N(1)	3966(3)	2345(1)	419(5)	3.5(1)
O(3)	6969(4)	3379(2)	3202(12)	8.3(2)
O(4)	6148(2)	2686(1)	−1441(5)	3.9(1)
C(1)	5247(4)	3005(1)	−1397(6)	3.5(1)
C(2)	3630(4)	3245(2)	1635(6)	3.9(1)
O(5)	5327(5)	3448(2)	−2308(8)	7.7(1)
C(3)	8664(4)	4144(1)	3519(6)	3.3(1)
C(4)	3915(3)	2898(1)	−323(6)	3.3(1)
C(5)	8296(6)	4324(2)	1530(7)	5.1(1)
C(6)	8727(9)	4824(3)	915(11)	7.6(2)
C(7)	9467(5)	4435(2)	4904(9)	5.4(1)
C(8)	9463(10)	5118(2)	2290(15)	8.5(2)
C(9)	9853(9)	4922(2)	4299(14)	8.1(2)
C(10)	3258(5)	3810(2)	1167(9)	4.9(1)
C(11)	3131(9)	4091(3)	3335(14)	8.6(2)
C(12)	1994(9)	3858(3)	−152(14)	8.4(2)
O(6)	6105(3)	2298(2)	−6526(5)	4.7(1)

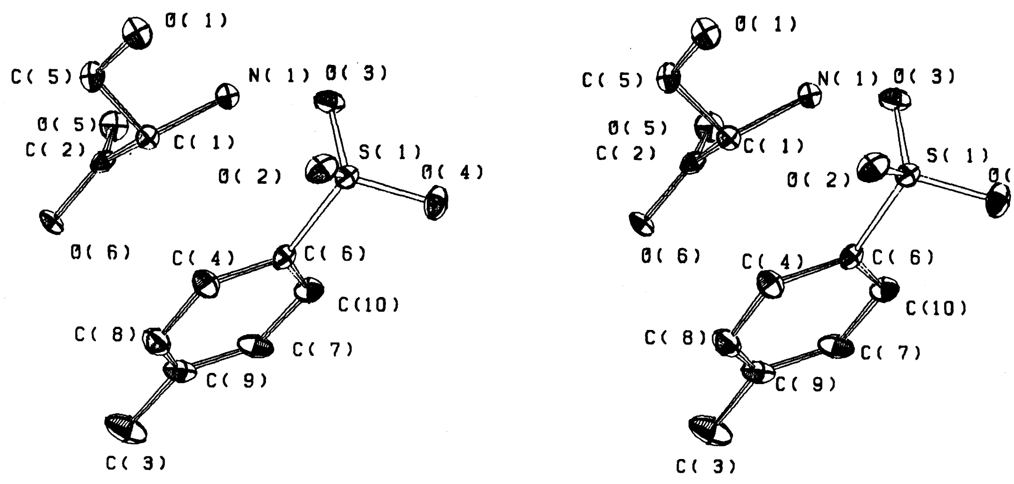

Fig. 1. Labeled stereoscopic drawing of **1**.

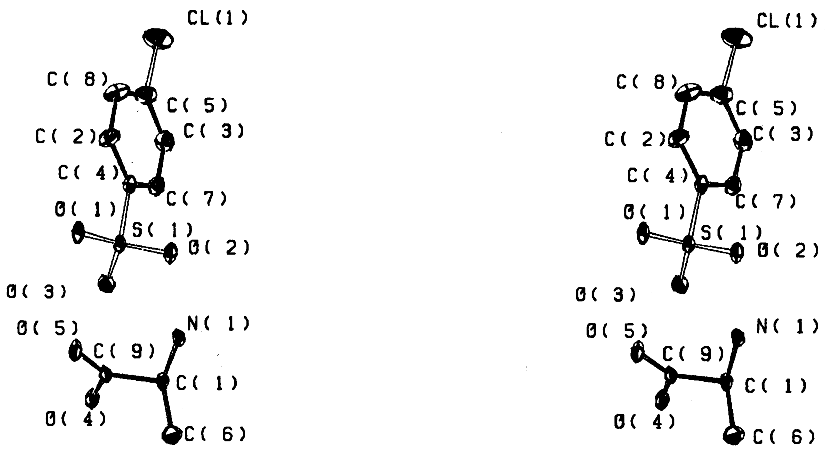

Fig. 2. Labeled stereoscopic drawing of **2**.

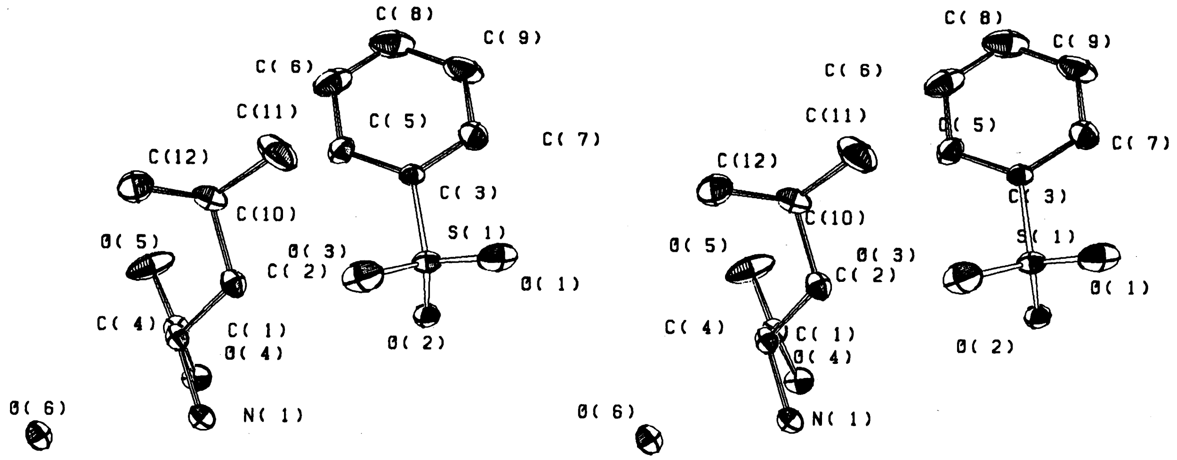

Fig. 3. Labeled stereoscopic drawing of **3**.

stereoscopic drawings of the crystals of **1**, **2**, and **3** are given in Figs. 1, 2, and 3, respectively. Their bond distances and angles are given in Tables 5, 6, and 7, respectively.

In the crystal of **1**, there are three distinct hydrogen bonds, by which two amine components and two acid components form a helical column along the *c* axis (Fig. 4). Moreover, two other hydrogen bonds exist. One links up the hydroxyl group in a molecule of serine with the carboxyl group in the neighboring molecule of serine. They are related by the operation: $x, y, -1+z$. And the other exists between the carboxyl group in serine and the oxygen atom in *p*-toluenesulfonic acid to combine two neighboring columns which are related by the operation: $-1+x, y, -1+z$. The geometries of the hydrogen bonds are listed in Table 8. There is no unusually short contact other than the hydrogen bonds.

In the crystal of **2**, two amine components and two acid components are also arranged to form a helical column by four distinct hydrogen bonds along the *a*

Table 5. Bond Distances (l/Å) and Angles (ϕ/°) of **1**

S(1)-O(2)	1.456(5)	O(2)-S(1)-O(3)	114.1(3)
S(1)-O(3)	1.456(5)	O(2)-S(1)-O(4)	112.6(3)
S(1)-O(4)	1.459(5)	O(2)-S(1)-C(6)	107.7(3)
S(1)-C(6)	1.739(5)	O(3)-S(1)-O(4)	110.8(3)
C(1)-N(1)	1.488(7)	O(3)-S(1)-C(6)	104.7(3)
C(1)-C(2)	1.512(8)	O(4)-S(1)-C(6)	106.3(3)
C(1)-C(5)	1.532(9)	N(1)-C(1)-C(2)	109.0(4)
O(1)-C(5)	1.389(8)	N(1)-C(1)-C(5)	109.4(4)
C(2)-O(5)	1.192(7)	C(2)-C(1)-C(5)	108.8(5)
C(2)-O(6)	1.298(8)	C(1)-C(2)-O(5)	121.7(5)
C(3)-C(9)	1.513(14)	C(1)-C(2)-O(6)	111.8(5)
C(4)-C(6)	1.406(8)	O(5)-C(2)-O(6)	126.5(6)
C(4)-C(8)	1.388(11)	C(6)-C(4)-C(8)	118.9(6)
C(6)-C(10)	1.401(8)	C(1)-C(5)-O(1)	112.5(5)
C(7)-C(9)	1.371(11)	S(1)-C(6)-C(4)	121.2(4)
C(7)-C(10)	1.408(10)	S(1)-C(6)-C(10)	119.0(4)
C(8)-C(9)	1.374(12)	C(4)-C(6)-C(10)	119.5(5)
		C(9)-C(7)-C(10)	121.3(7)
		C(4)-C(8)-C(9)	122.3(8)
		C(3)-C(9)-C(7)	118.4(8)
		C(3)-C(9)-C(8)	122.7(8)
		C(7)-C(9)-C(8)	118.9(7)
		C(6)-C(10)-C(7)	119.1(6)

Table 6. Bond Distances (l/Å) and Angles (ϕ/°) of **2**

S (1)-O(1)	1.451(5)	O (1)-S (1)-O(2)	112.0(2)
S (1)-O(2)	1.469(4)	O (1)-S (1)-O(3)	113.6(3)
S (1)-O(3)	1.439(4)	O (1)-S (1)-C(4)	105.9(2)
S (1)-C(4)	1.778(5)	O (2)-S (1)-O(3)	112.9(2)
Cl(1)-C(5)	1.753(8)	O (2)-S (1)-C(4)	104.5(2)
C (1)-N(1)	1.487(7)	O (3)-S (1)-C(4)	107.1(2)
C (1)-C(6)	1.515(10)	N (1)-C(1)-C(6)	110.1(5)
C (1)-C(9)	1.503(8)	N (1)-C(1)-C(9)	108.0(4)
O (4)-C(9)	1.315(7)	C (6)-C(1)-C(9)	111.0(5)
C (2)-C(4)	1.389(9)	C (4)-C(2)-C(8)	119.7(7)
C (2)-C(8)	1.379(12)	C (5)-C(3)-C(7)	119.9(7)
C (3)-C(5)	1.360(10)	S (1)-C(4)-C(2)	119.5(4)
C (3)-C(7)	1.367(9)	S (1)-C(4)-C(7)	120.0(4)
O (5)-C(9)	1.206(7)	C (2)-C(4)-C(7)	120.5(5)
C (4)-C(7)	1.372(8)	Cl(1)-C(5)-C(3)	119.0(6)
C (5)-C(8)	1.382(12)	Cl(1)-C(5)-C(8)	119.3(6)
		C (3)-C(5)-C(8)	121.6(7)
		C (3)-C(7)-C(4)	119.8(6)
		C (2)-C(8)-C(5)	118.4(8)
		C (1)-C(9)-O(4)	112.8(5)
		C (1)-C(9)-O(5)	122.1(5)
		O (4)-C(9)-O(5)	125.0(5)

Table 7. Bond Distances (l/Å) and Angles (ϕ/°) of **3**

S (1)-O(1)	1.431(5)	O(1)-S (1)-O(2)	113.1(3)
S (1)-O(2)	1.458(3)	O(1)-S (1)-O(3)	113.8(4)
S (1)-O(3)	1.460(7)	O(1)-S (1)-C(3)	107.1(3)
S (1)-C(3)	1.763(4)	O(2)-S (1)-O(3)	109.2(3)
N(1)-C(4)	1.498(5)	O(2)-S (1)-C(3)	106.2(2)
O(4)-C(1)	1.216(5)	O(3)-S (1)-C(3)	107.0(3)
C(1)-O(5)	1.274(6)	O(4)-C(1)-O(5)	123.3(4)
C(1)-C(4)	1.506(5)	O(4)-C(1)-C(4)	122.1(3)
C(2)-C(4)	1.535(5)	O(5)-C(1)-C(4)	114.5(4)
C(2)-C(10)	1.528(7)	C(4)-C(2)-C(10)	116.5(4)
C(3)-C(5)	1.370(7)	S (1)-C(3)-C(5)	120.1(3)
C(3)-O(7)	1.391(6)	S (1)-C(3)-O(7)	117.8(3)
C(5)-C(6)	1.411(11)	C(5)-C(3)-O(7)	122.0(4)
C(6)-C(8)	1.354(13)	N(1)-C(4)-C(1)	106.3(3)
O(7)-C(9)	1.364(10)	N(1)-C(4)-C(2)	108.3(3)
C(8)-C(9)	1.402(13)	C(1)-C(4)-C(2)	114.0(3)
C(10)-C(11)	1.535(10)	C(3)-C(5)-C(6)	118.2(6)
C(10)-C(12)	1.504(10)	C(5)-C(6)-C(8)	120.2(8)
		C(3)-O(7)-C(9)	119.0(6)
		C(6)-C(8)-C(9)	120.6(9)
		O(7)-C(9)-C(8)	119.9(8)
		C(2)-C(10)-C(11)	107.6(5)
		C(2)-C(10)-C(12)	112.6(5)
		C(11)-C(10)-C(12)	111.8(6)

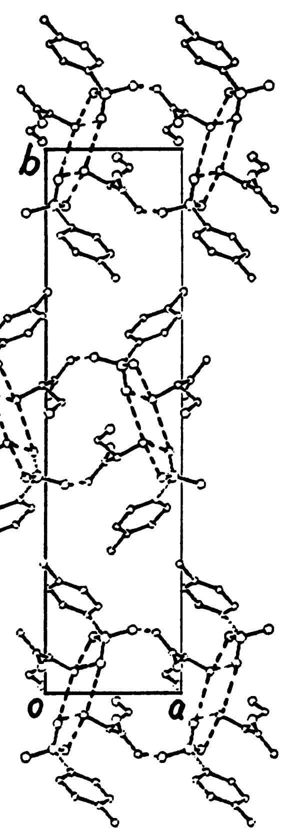

Fig. 4. The crystal structures of **1** viewed along the c axis. Hydrogen bonds are shown by dashed lines.

Table 8. The Distances (l/Å) of O···N or O···O, and Angles (ϕ/°) of ∠O···H-N or ∠O···H-O

	Distance	Angle
1:		
O(2)···H-N(1)^{i}	2.929(6)	155(0)
O(3)···H-N(1)^{ii}	2.764(6)	158(5)
O(3)···H-N(1)^{iii}	2.855(6)	177(0)
O(4)···H-O(6)^{iv}	2.608(7)	157(6)
O(5)···H-O(1)^{v}	2.703(6)	169(7)
2:		
O(1)···H-N(1)^{vi}	2.839(7)	168(0)
O(2)···H-N(1)^{i}	2.922(6)	162(1)
O(2)···H-O(4)^{vii}	2.646(6)	178(8)
O(3)···H-N(1)^{v}	2.995(7)	180(1)
3:		
O(6)···H-N(1)^{ii}	2.850(5)	176(0)
O(6)···H-O(3)^{ii}	2.915(8)	163(5)
O(1)···H-O(5)^{ii}	2.820(7)	154(8)
O(2)···H-O(3)^{viii}	2.836(5)	157(6)
O(2)···H-N(1)^{viii}	2.836(5)	165(0)
O(4)···H-N(1)^{viii}	2.868(5)	156(0)

The symmetry operations: i: x, y, z; ii: x, y, $1+z$; iii: $3/2-x$, $1-y$, $1/2+z$; iv: $-1+x$, y, $-1+z$; v: x, y, $-1+z$; vi: $-1/2+x$, $3/2-y$, $1-z$; vii: $1/2+x$, $3/2-y$, $-z$; viii: $1/2+x$, $1/2-y$, $-z$.

axis (Fig. 5). The geometries of the hydrogen bonds are also listed in Table 8. Other than the hydrogen bonds, there is no unusually short nonbonding distance.

In the crystal of **3**, two amine components and two acid components show the same arrangement to form a helical column by four distinct hydrogen bonds along the a axis (Fig. 6). In addition, one molecule of water per one molecule of salt is included in the crystal of **3** to form two more hydrogen bonds. No unusually short contact exists other than the hydrogen bonds. The geometries of the hydrogen bonds are listed in Table 8.

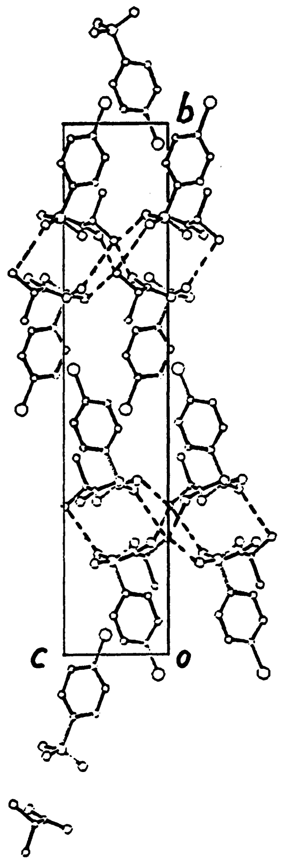

Fig. 5. The crystal structures of **2** viewed along the *a* axis. Hydrogen bonds are shown by dashed lines.

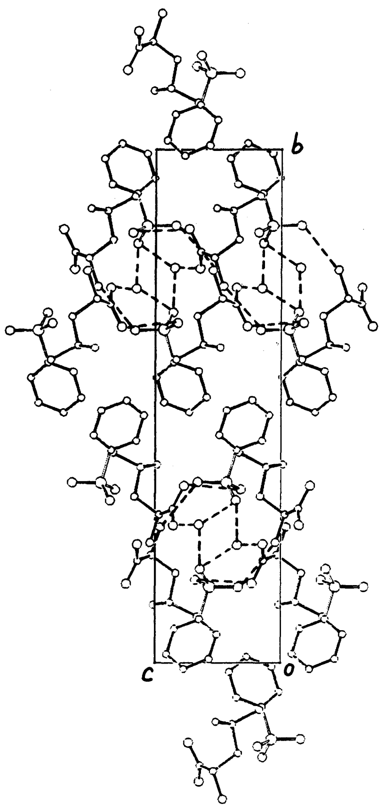

Fig. 6. The crystal structures of **3** viewed along the *a* axis. Hydrogen bonds are shown by dashed lines.

Crystals of **1**, **2**, and **3** are built up, in a similar fashion, by three distinct hydrogen bonds between two amine components and two acid components to form helical columns along the axis. This structural similarity is also observed for the crystals of cinnamic acid salts of (*R*)-1-phenylethylamine (**4**) and of (*R*)-1-(4-isopropylphenyl)ethylamine (**5**).[2] Figure 7 shows the helical columns in **1**, **2**, **3**, **4**, and **5**. Every helical column is found to be supported by repeating helical hydrogen networks.

The crystal of **1** has the same repeating unit as those of the crystals of **4** and **5**, containing one nitrogen in a molecule of the amine component and two oxygens in a molecule of the acid component. The crystal of **1** also has another hydrogen bond, which combines the amine component with the acid component, to fix the column tightly as observed in the crystals of **4** and **5**. Moreover, in the case of the crystal of **1**, one more distinct hydrogen bond exists between the carboxyl group in the amino acid component and the hydroxyl group in the neighboring acid component. They are related by the operation: x, y, $-1+z$. On the other hand, in the crystals of **2** and **3**, the repeating unit includes uniquely a part of amino acids (N–C–C–O). To support the helical hydrogen networks in each column tightly, another distinct hydrogen bond exists between two amino acid components. The repeating units and the supporting hydrogen bonds in each crystal are denoted by dashed and waved lines, respectively, in Fig. 7.

The analyses of these crystals show that conglomerate crystals of amino acid salts include a unique part of the amino acid (N–C–C–O) in the helical column, except for the case like **1** with the hydroxyl group, which can make hydrogen bonds. But, as shown in Fig. 7, the alternate arrangement of the arenesulfonic acid and the amino acid components in the crystals of **1**, **2**, and **3** is essentially the same as those of cinnamic acid and the amine components in the crystals of **4** and **5**. Moreover, arenesulfonic acid is also a rigid molecule like cinnamic acid. The rigidity would prevent the molecule of the amino acid from contacting each other by strong hydrogen bonds.

The appropriate R^1 and R^2 groups tightly pack two neighboring columns, which are related by twofold screw axis. The schematic drawing is shown in Fig. 8. The helical column is denoted by the thick line. Benzene rings in neighboring columns are arranged parallel each other to interact by π–π orbitals. The π–π interaction is denoted by dashed line. Compared with the crystal of **3**, the crystal of **2** has leucine bigger than that of alanine, and benzenesulfonic acid smaller than *p*-chlorobenzenesulfonic acid. The fact suggests that

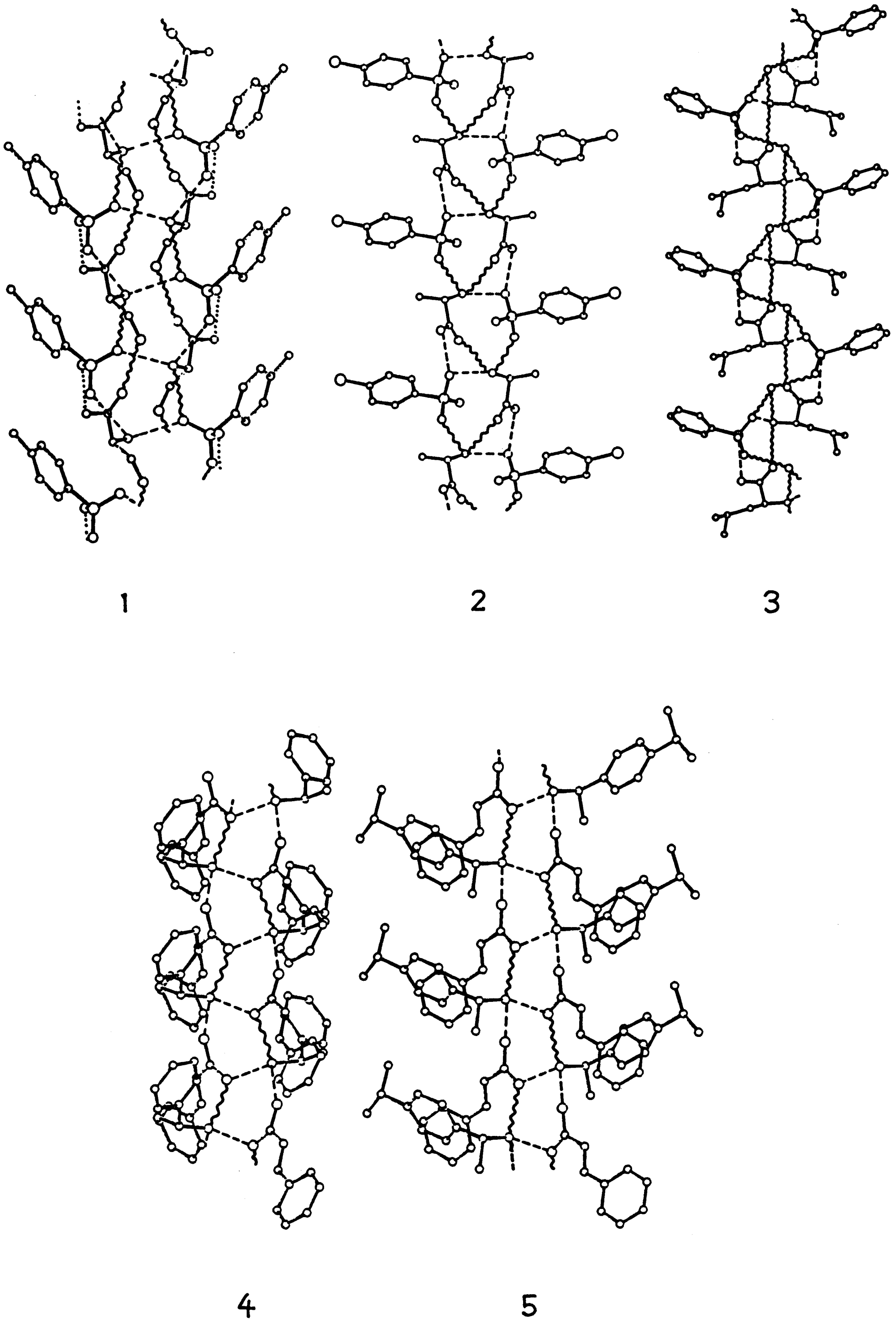

Fig. 7. A helical column in each crystal of **1**, **2**, **3**, **4**, and **5**. Hydrogen bonds are shown by dashed, waved and dotted lines. **1**: *p*-toluenesulfonic acid salt of L-serine, **2**: *p*-chlorobenzenesulfonic acid salt of L-alanine, **3**: benzenesulfonic acid salt of L-leucine, **4**: cinnamic acid salt of 1-phenylethylamine, **5**: cinnamic acid salt of 1-(4-isopropylphenyl)ethylamine.

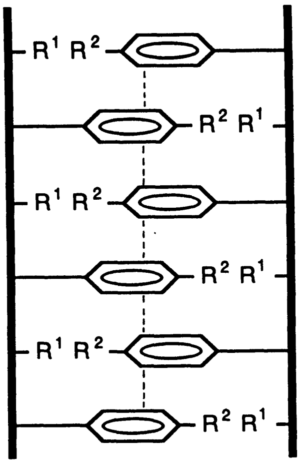

Fig. 8. The schematic drawing of the helical column. **1**: R^1=H and R^2=Me. **2**: R^1=Me and R^2=Cl. **3**: R^1=H and R^2=Pr^i. **4**: R^1=H and R^2=Ph **5**: R^1=H and R^2=$C_6H_4Pr^i$-*p*.

bigger R^1 paired with smaller R^2 makes the crystal packing close by π–π interaction. In the crystal of **1**, R^1 is rather small because hydroxymethyl group is oriented along the column by a hydrogen bond, and paired acid has methyl group bigger than hydrogen as R^2.

These results indicate that the shape of the arenesulfonic acid plays an important role to form a rigid helical arrangement and to offer suitable space for the amino acid molecule. Namely, the following criteria proposed by us are considered to be appropriate for the choice of an achiral derivatizing agent in the transformation of a racemic compound into a conglomerate crystal: (a) The achiral derivatizing agent should be able to form a helical column by hydrogen bonds with the molecule of the racemic compound; (b) The derivatizing agent should be rigid and flat to limit the orientation of the molecules of the racemic compound; (c) The sizes of the derivatizing agent and the molecule of the racemic compound should be complementary to make the crystal packing close.

A part of this work was supported by The Fujisawa Foundation, to which acknowledgment is made.

References

1) J. Jacques, A. Collet, and S. H. Wilan, "Enantiomers, Racemates, and Resolutions," John Wiley & Sons, New York (1981).

2) K. Saigo, H. Kimoto, H. Nohira, K. Yanagi, and M. Hasegawa, *Bull. Chem. Soc. Jpn.*, **60**, 3655 (1987).

3) I. Chibata, S. Yamada, M. Yamamoto, and M. Wada, *Experientia*, **24**, 638 (1968).

4) N. Sato, T. Uzuki, K. Toi, and T. Akashi, *Agr. Biol. Chem.*, **33**, 1107 (1969).

5) S. Yamada, M. Yamamoto, and I. Chibata, *Chem. Eng. (London)*, June 2, 528 (1973).

6) S. Yamada, M. Yamamoto, and I. Chibata, *J. Org. Chem.*, **38**, 4408 (1973).

7) P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson, "A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, MULTAN 78," University of York, England, and Louvain, Belgium (1978).

8) G. M. Sheldrick, "Program for Crystal Structure Determination, SHELX 76," University of Cambridge, England (1976).

9) "International Tables for X-ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1974).

10) F_o—F_c tables, anisotropic thermal temperature factors and fractional atomic coordinates of hydrogen atoms are deposited as Document No. 8881 at the Office of the Editor of Bull. Chem. Soc. Jpn.

11) The equivalent isotropic temperature factors were computed using the following expression;

$$B_{eq} = 4/3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2).$$