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Crystal Structure of Alkylammonium Salts of *N,N'*-Oxalylbis(phenylglycine)s: Optional Construction of a Monolayer or Bilayer Structure

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Abstract: *meso-N,N'*-Oxalylbis(phenylglycine) (*meso*-**1**) reacts with 1-phenyl-2-methylpropylamine (**2a**) to construct a monolayer structure in crystals. On the other hand, (*R,R*)-*N,N'*-oxalylbis(phenylglycine) [(*R,R*)-**1**] reacts with 1-phenylethylamine (**2b**) to construct a bilayer structure in crystals. X-ray crystallographic study of the two salts elucidated that these layer structures were attributed to the rigid oxalamide functionality and hydrogen bonding of the salt, and optional formation of two types of layers was induced by the stereochemistry of the phenylglycine.

Keywords: amino acids and derivatives; ammonium salts; stereochemistry; X-ray crystal structures

To date, crystal engineering to design and control the packing arrangement of molecules in solid state has been well investigated. Although one may design and prepare molecules, which will self-assemble into crystalline solids with the desired structural features, by combining their chemical properties with symmetry considerations, this process is very difficult because of a multitude of inherent problems. Despite these problems, much progress has been made and many groups have completed successful supramolecular synthesis. One successful approach is to design a two-dimensional network of mutually hydrogen bonded molecules to form a sheet. The sheets assemble in the third dimension to stack as either single layers or bilayers. The bilayer structures are found in crystalline solids of such amphiphilic compounds as bile acids,[1a] calixarenes,[1b] and peptides.[1c] Recently, Ward et al. reported guanidium alkane- and arenesulfonates which construct a monolayer or bilayer structure depending on the size of the alkane and arene moieties.[2a] It was also reported by Lewis and his coworkers that, in naphthalenedicarboxamide crystals, a monolayer or bilayer structure is chosen by the positions of their substituents.[2b]

Here we wish to report optional construction of the monolayer or bilayer structure in the crystalline salt of *N,N'*-oxalylbis(phenylglycine) (**1**) and α–alkylbenzylamine (**2**), *which*

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accords with the stereochemistry of 1.[3] If the phenyl group of the amine (**2**) which can bind two molecules of **1** stands perpendicular to the oxalamide plane, the packed amphiphilic layer will construct either a mono- or bilayer structure (Fig. 1).

It is well-known that oxalyldiamino acids and their esters give rise to two-dimensional layered crystals, in which the central oxalamide (-NH-CO-CO-NH-) unit generally adopts a near-perfect planar and *trans* conformation via pseudo-C5-type intramolecular hydrogen bonding.[4,5] When the oxalyldiamino acid forms a salt with an amine, the resulting anionic carboxylate oxygens are anticipated to contact more strongly with the amide proton *via* an intramolecular hydrogen bonding. This speculation was supported by MNDO/PM3 calculation; the most stable conformations of (*R*,*R*)-**1** and its dianion are shown in Figure 2.[6] Hence, two phenyl groups of **1** are suggested to be located at the opposite or same side of the oxalamide plane of the *meso* or (*R*,*R*)- **1**, respectively, in the case of the salt formation with **2**.

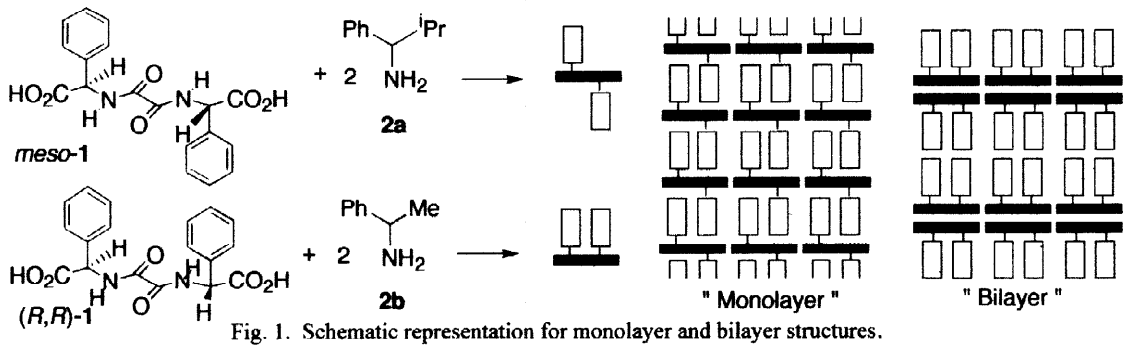

Fig. 1. Schematic representation for monolayer and bilayer structures.

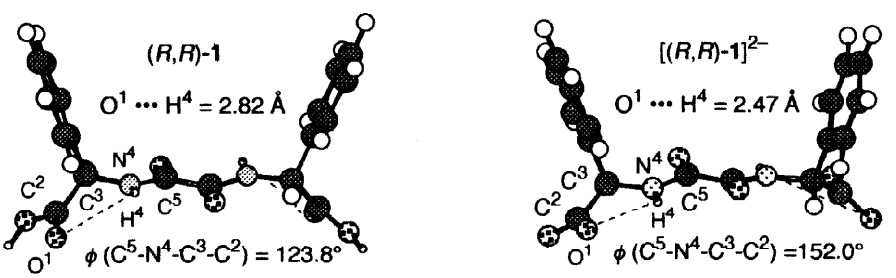

Fig. 2. Most stable conformations of (*R*,*R*)-**1** and its dianion calculated by MNDO/MP3.

First, *meso*-**1** reacted with 1-phenyl-2-methylpropylamine **2a** to form the corresponding salt, and recrystallization of the salt afforded a single crystal.[7] The salt of *meso*-**1** with **2a** is centrosymmetric and has a monolayer structure (Fig. 3a). Hydrophobic moieties such as phenyl and alkyl groups are arranged on both sides of one hydrogen bonding layer. The hydrogen bonding network is shown in Figure 3b. The oxalamide functionality has a complete *trans* conformation (the torsion angle of O^2-C^9-C^{*9}-O^{*2}; 180.0°).[10] The salt between the amino and carboxyl groups formed a 12-membered ring, where bond distances are 2.74 (N^1•••O^3) and 2.83 (N^1•••O^5) Å.[11] Furthermore, one ammonium hydrogen is bound to an oxygen of the oxalyl group 2.80 (N^1•••O^2) Å to allow the two-dimensional monolayer structure.

We obtained a single crystal of the salt of (*R*,*R*)-**1** with 1-phenylethylamine **2b**, which was suitable for X-ray crystallography.[7] The crystal consists of (*R*,*R*)-**1**, (*R*)-**2b**, (*S*)-**2b**, and water. The salt of (*R*,*R*)-**1** with **2b** formed a bilayer structure, in which hydrophobic moieties such as phenyl and alkyl groups are located on only one side of the layer (Fig. 4).

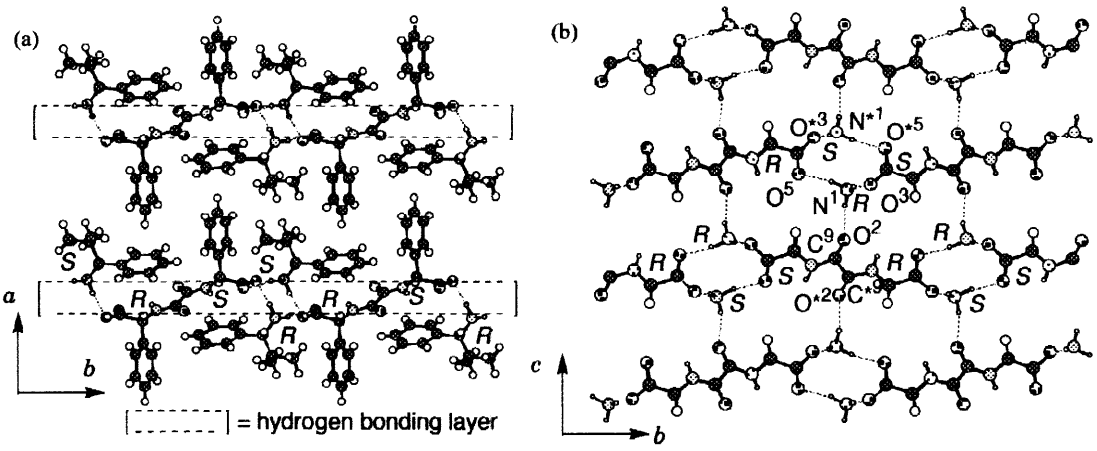

Fig. 3. Crystal packing of the salt of *meso*-**1** with **2a**. (a) A monolayer structure (*a*-*b* plane). (b) The hydrogen bonding layer structure (*b*-*c* plane). Alkyl and phenyl groups are omitted.

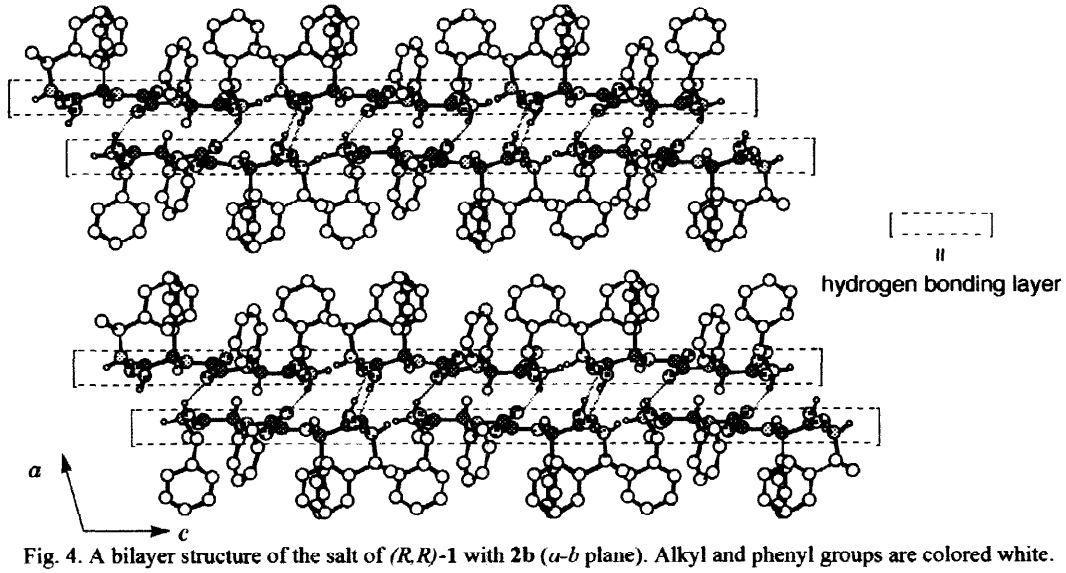

Fig. 4. A bilayer structure of the salt of *(R,R)*-**1** with **2b** (*a*-*b* plane). Alkyl and phenyl groups are colored white.

As shown in Figure 5a, the oxalamide moiety has a *trans* conformation which is somewhat distorted (the torsion angle of O^7-C^{11}-C^{13}-O^4; 170.5°).[10] But, in the crystal packing, this dianionic (*R,R*)-**1** has a more planar structure (the torsion angles of C^{20}-C^{12}-N^{54}-C^{11} and C^{21}-C^{15}-N^{10}-C^{13}; 161.4° and 169.0°, respectively) than the calculated conformation (152.0°) of Figure 1. The arrangement of amino and carboxyl groups constructed a 12-membered ring in the salt; bond distances are 2.83 (N^6•••O^1), 2.72 (N^6•••O^{14}), 2.73 (N^8•••O^2), and 2.91 (N^8•••O^3) Å.[11] A water molecule joins the amino group and the carboxyl group (N^8•••O^9; 2.89 and O^1•••O^9; 2.83Å), which plays an important role in the formation of a rigid layer structure.

Two amphiphilic layers combined face-to-face via two hydrogen bonds (Fig. 5b); one hydrogen bond between water and the carboxylate is 2.76 Å (O^9•••O^3) and the other one is between an ammonium and an oxygen of the oxalyl group 2.87 Å (N^6•••O^4).

In conclusion, we elucidated that a central oxalamide functionality of *N,N'*-oxalylbis(phenylglycine) (**1**) is essential to the conformational *trans* fixation to construct a rigid layer and stereochemistry of the phenylglycine part is crucial for the optional construction of a bilayer or monolayer structure. These results suggest that the chiral amino

acid molecule serves as a useful building block for a well-designed crystal structure.

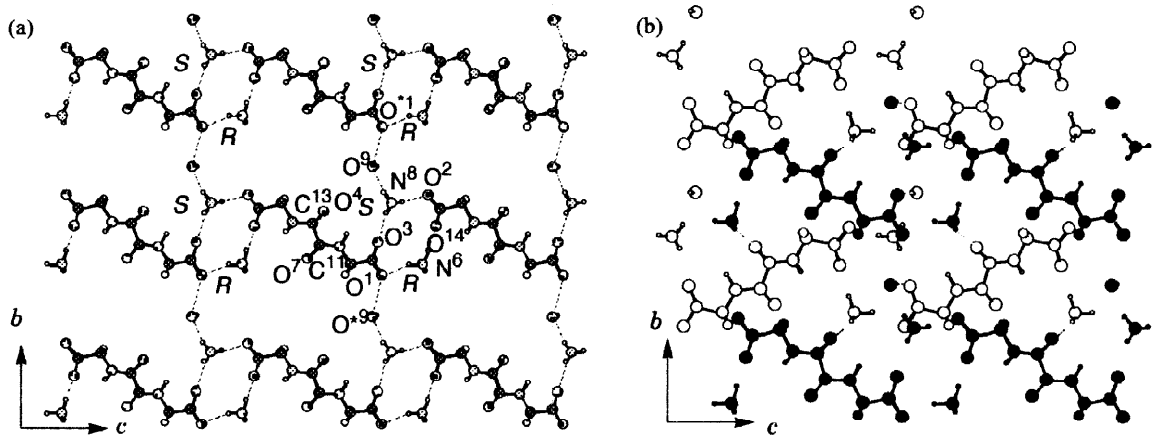

Fig. 5. (a) The hydrogen bonding layer of the salt of *(R,R)*-**1** with **2b** (*b-c* plane). (b) The offset between two layers (*b-c* plane). Alkyl and phenyl groups are omitted.

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[3] (*R,R*)-**1**: white powder, mp. 205 ℃ (decomp.), IR (KBr): 3600-3200, 1725, 1656, 1499, 1457, 1411, 1294, 1247, 1091, 745, 702 cm^{-1} ^{1}H-NMR(300 MHz: d4-MeOH): 5.33 (s, 2H, NC*H*), 7.26-7.45 (m, 10H, Ph). *meso*-**1**: white powder, mp. 225 ℃ (decomp.), $[\alpha]^{25}_D$ = -231.52 (c = 1.01, MeOH) IR (KBr): 3300, 1718, 1660, 1506, 1416, 1224, 1088, 1064, 966, 848, 726 cm^{-1} ^{1}H-NMR(300 MHz: d6-DMSO): 5.42 (d, J = 7.66 Hz, 2H, NC*H*), 7.30-7.42 (m, 10H, Ph), 9.02(d, J = 7.66 Hz, 2H, N*H*).

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[7] A Mac Science MXC18 four-circle diffractometer and Cu Kα (λ = 1.54178) radiation was used. The structures were solved and refined by direct methods (SIR 92[8] on a computer program package; CRYSTAN-GM ver. 6.2.1 from MAC Science Co. Ltd.) Further detailed data have been deposited with the Cambridge Crystallographic Data Centre.[9]
Crystal data for the salt of *meso*-**1** and 1-phenyl-2-methylpropylamine **2a**: $C_{38}H_{46}N_4O_6$, M 654.80. Monoclinic, *P* $2_1/c$ (No 14), a = 11.898(3) Å, b = 12.919(3) Å, c = 11.731(3) Å, β = 101.63(2), V = 1766.2(8) $Å^3$, Z = 2, Dcalcd = 1.23, T = 298 K, 3819 Reflections measured, 3366 independent. *R* = 0.0457 (1801 reflections with Fo > 3σ(Fo)), *Rw* = 0.0513, with heavy atoms refined anisotropically, residual electron density 0.27/-0.23.
Crystal data for the salt of (*R,R*)-**1** and 1-phenylethylamine **2b** with water: $C_{34}H_{40}N_4O_7$, M 616.71. Monoclinic, $P2_1$(No 4), a = 14.605(3) Å, b = 10.034(3) Å, c = 12.129(3) Å, β = 104.44(2)°, V = 1721.5(8) $Å^3$, Z = 2, Dcalcd = 1.19, T = 298 K, 3724 Reflections measured, 3468 independent. *R* = 0.0446 (3040 reflections with Fo > 3σ(Fo)), *Rw* = 0.0519, with heavy atoms refined anisotropically, residual electron density 0.15/-0.22.
Powder X-ray analyses support that both **2b** salt of *meso*-**1** and **2a** salt of (*R,R*)-**1** construct some layer structures without the aid of water, which are confirmed by elemental analysis. But, single crystals suitable for X-ray analysis were not obtained.

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