



# Article Reversible Single-Crystal-to-Single-Crystal Phase Transition of Chiral Salicylidenephenylethylamine

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Abstract: The chiral crystal of enantiomeric (*S*)-*N*-3,5-*di*-tert-butylsalicylidene-1-phenylethylamine in the enol form [enol-(*S*)-1] undergoes a reversible single-crystal-to-single-crystal (SCSC) phase transition at  $T_c \approx 3 \,^{\circ}$ C from the room temperature  $\alpha$ -form in orthorhombic space group  $P2_12_12_1$ (Z' = 1) to the low temperature  $\beta$ -form in the monoclinic space group  $P2_1$  (Z' = 2) with a thermal hysteresis of approximately 1.7  $^{\circ}$ C. A detailed comparison of the crystal structures of the  $\alpha$ - and  $\beta$ -forms revealed that the 5-*tert*-butyl group of one molecule in the asymmetric unit of the  $\beta$ -form rotated by ca. 60°, and the dihedral angle between the phenyl and salicyl planes increased slightly in the  $\beta$ -form crystal. However, the changes in the molecular conformation and packing arrangement are small, which leads to the reversible SCSC phase transition with no destruction of the crystal lattice. The dielectric constant along the *b*-axis was small, probably due to the weak intermolecular interactions in the crystals.

**Keywords:** reversible single-crystal-to-single-crystal phase transition; enantiomeric (*S*)-salicylidenephenylethylamine; dielectric properties

# 1. Introduction

A single-crystal-to-single-crystal (SCSC) phase transition is defined as a micro-mutual transformation in crystal structure with no destruction of the crystal lattice. A reversible SCSC phase transition can occur when the changes in the molecular conformation and packing arrangement in the crystal are very small at the phase transition, so there are no cracks or breaks in the crystal. Hence, the reversible SCSC phase transition is a fascinating phenomenon because of its potential applications in ferroelectric and switchable dielectric devices [1–3]. Several molecular crystals that undergo temperature-induced reversible SCSC phase transition have been reported [4–10].

Chiral (*S*)-*N*-3,5-*di*-*tert*-butylsalicylidene-1-phenylethylamine in the enol-form [enol-(*S*)-1] has a photochromic nature in the crystalline state caused by photoinduced proton transfer [11]. The plate-like enol-(*S*)-1 crystals bend reversibly upon ultraviolet (UV) irradiation [12]. Recently, we reported the chiroptical and optical anisotropic properties of photomechanical enol-(*S*)-1 crystals before and under UV irradiation [13]. In the course of this study, we discovered that the chiral enol-(*S*)-1 (Scheme 1) crystal underwent a reversible SCSC phase transition from the room temperature

 $\alpha$ -form to the low-temperature  $\beta$  form at approximately 3 °C. This reversible SCSC phase transition is a rare occurrence because it occurs between two enantiomorphic phases, which also mean noncentrosymmetric phases. The properties such as ferroelectricity, piezoelectricity, and second-order optical nonlinearlity are allowed in a noncentrosymmetric structure. Other noncentrosymmetric SCSC transitions have been previously reported [14]. We discuss a possible mechanism for the enantiomorphic SCSC phase transition based on the crystal structure changes between the  $\alpha$ - and  $\beta$ -forms. The temperature dependence of the dielectric constant in the single crystalline state was also measured.



Scheme 1. Enantiomeric (S)-salicylidenephenylethylamine [enol-(S)-1].

# 2. Results and Discussion

The compound enol-(*S*)-1 was synthesized as reported previously [15]. Single crystals were obtained by slow evaporation of a solution in 2-propanol at room temperature. Differential scanning calorimetry (DSC) of enol-(*S*)-1 was performed over the temperature range from 10 to -10 °C at a rate of 2 °C·min<sup>-1</sup> with cooling initially and then heating (Figure 1). Cooling the crystalline sample of enol-(*S*)-1 had an exothermic peak at 2.2 °C. The phase transition started at 2.7 °C and ended at 0.1 °C. Heating the crystalline sample of enol-(*S*)-1 had an endothermic peak at 3.9 °C. The reverse phase transition began at 3.6 °C and ended at 4.8 °C. The sharp shapes of these two peaks and the thermal hysteresis of 1.7 °C reveal a first-order phase transition. The enthalpy at the exothermic and endothermic peaks was -0.69 and 0.67 kJ·mol<sup>-1</sup>, respectively. This small thermal hysteresis might be a general feature of SCSC transition because small hysteresis was reported also in the previous papers [4,7,10]. DSC curves in wide temperature ranges indicated no existence of additional phase transition (Figure S1).



Figure 1. DSC curves of enol-(S)-1 crystal on initial cooling and then heating.

Figure 2 shows the variable-temperature unit cell determination of enol-(*S*)-1 using a single crystal over the temperature range from -50 to +50 °C at 10 °C intervals with initial heating and then

cooling. The length of the *a*-axis changed discontinuously between 0 and 10 °C on heating and cooling; the differences were 0.06 and 0.07 Å, respectively (Figure 2a). Angle  $\beta$  also changed reversibly from 90° to 92° between 0 °C and 10 °C on heating and cooling (Figure 2d). The length of the *c*-axis and the volume did not change significantly between 0 °C and 10 °C (Figure 2c,e). In contrast, the length of the *b*-axis changed continuously on both heating and cooling (Figure 2b). The single crystal maintained its transparency without cracking after the heating and cooling cycles, revealing that the phase transition proceeded reversibly via a single crystalline state.



**Figure 2.** Temperature dependence of the lattice constants of enol-(*S*)-**1** single crystal on initial heating and then cooling; lengths of the (**a**) *a*-, (**b**) *b*-, and (**c**) *c*-axes, (**d**) angle  $\beta$ , and (**e**) volume.

X-ray crystallographic analysis of enol-(*S*)-1 was performed at 10 °C and -50 °C (Table 1). The  $\alpha$ -form (10 °C) crystallizes in the orthorhombic space group  $P2_12_12_1$ , which is similar to the finding in a previous report [12]. The  $\beta$ -form (-50 °C) belongs to the monoclinic space group  $P2_1$ . After the phase transition from the  $\alpha$ -form to the  $\beta$ -form, the lengths of the *a*- and *b*-axes decreased by -0.09927 Å (-1.57%) and -0.2352 Å (-0.67%), respectively, while that of the *c*-axis increased by +0.04083 Å (+0.41%). Overall, the volume decreased by -42.51 Å<sup>3</sup> (-1.94%). The powder X-ray diffraction (XRD) pattern at room temperature was coincident with the calculated XRD pattern from the single crystal structure of the  $\alpha$ -form, revealing no existence of additional phase transition (Figure S2).

<b>Fable 1.</b> Crysta	l data for en	ol-(S)-1 crystals
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	α-Form	β-Form
Temperature (°C)	10	-50
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_{1}2_{1}2_{1}$	$P2_1$
a (Å)	6.3058 (4)	6.20653 (11)
b (Å)	35.071 (2)	34.8358 (7)
c (Å)	9.8851 (6)	9.92593 (18)
$\beta$ (deg)	90	92.7570 (10)
Volume (Å <sup>3</sup> )	2186.1 (2)	2143.59 (7)
Ζ	4	4
$\rho_{\rm calc}  (\rm g \cdot \rm cm^{-3})$	1.025	1.046
$R_1$ [I > 2 $\sigma$ (I)]	0.0681	0.0475
Goodness of fit	1.052	1.030

Figure 3 shows the Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawings and molecular conformations of the  $\alpha$ - and  $\beta$ -form crystals. There is one crystallographically independent molecule (A) in the  $\alpha$ -form crystal (Figure 3a); the 5-*tert*-butyl group (brown color) is disordered in the 0.217 occupancy. The  $\beta$ -form crystal consists of two crystallographically independent molecules (B and C) in the asymmetric unit (Figure 3b,c). The 5-*tert*-butyl groups (brown color) of both molecules are disordered in the 0.229 (B) and 0.245 (C) occupancies, respectively.



**Figure 3.** ORTEP drawings (**a**–**c**) at the 25% probability level, and the molecular conformations (**d**–**f**) of enol-(*S*)-**1** in the  $\alpha$ - and  $\beta$ -form crystals: (**a**,**d**) A molecule of  $\alpha$ -form, (**b**,**e**) B, and (**c**,**f**) C molecules of the  $\beta$ -form. The 5-*tert*-butyl groups (**brown**) are disordered in the 0.217 (**A**), 0.229 (**B**), and 0.245 (**C**) occupancies, respectively. The viewpoints of molecular conformations of the 5-*tert*-butyl groups are displayed in the ORTEP drawings with **black** solid arrows. The disordered 5-*tert*-butyl groups in minor occupancies and all hydrogen atoms in (**d**–**f**) are omitted for clarity.

In molecule A of the  $\alpha$ -form, an intramolecular hydrogen bond is formed between the N atom of the C=N Schiff base and the H atom of the 2-OH group of the salicyl ring (black dotted line in Figure 3a); the N—O distance is 2.591 Å and the N—H–O angle is 160.40°. In molecules B and C of the  $\beta$ -form, similar intramolecular hydrogen bonds (black dotted lines in Figure 3b,c) are formed with N—O distances of 2.596 and 2.591 Å and N—H–O angles of 148.67° and 148.94°, respectively.

The dihedral angle between the phenyl and salicyl plane in molecule A of the  $\alpha$ -form is 41.06°. The corresponding dihedral angles increase slightly to 46.82° and 43.97° in the B and C molecules of the  $\beta$ -form, respectively. The analogous salicylideneaniline crystals can cause a photochromic reaction when the dihedral angle between the phenyl and salicyl planes exceeds 30° [16]. Therefore, the  $\beta$ -form crystal should also have a photochromic nature to the *trans*-keto-form with UV irradiation.

The most significant change in the molecular conformation with the phase transition is that the 5-*tert*-butyl group (red color) of molecule C (Figure 3f) in the  $\beta$ -crystal rotates by around 60° from the original position (green) of molecule A (Figure 3d) in the  $\alpha$ -crystal, whereas the 5-*tert*-butyl group (green) of molecule B (Figure 3e) does not rotate. In comparison, the conformations of the 3-*tert*-butyl groups in molecules B and C do not change drastically from that in molecule A after the phase transition. The torsion angles are shown in Table 2.

	α-Form		β-Form	
	Molecule A	Molecule B	Molecule C	
Intramolecular hydrogen bond				
N—O distance (Å)	2.591	2.596	2.591	
N—H–O angle (deg)	160.4	148.67	148.94	
Dihedral angle between phenyl and salicyl plane (deg)	41.06	46.82	43.97	
Torsion angle (deg)				
5- <i>t</i> -Bu group	61.5	63.29	126.86	
	(C5-C6-C11-C13)	(C19-C20-C25-C27)	(C33-C34-C39-C42)	
	-59.21	-55.24	6.27	
	(C5-C6-C11-C14)	(C19-C20-C25-C28)	(C33-C34-C39-C40)	
	178.68	-175.97	-115.53	
	(C5-C6-C11-C12)	(C19-C20-C25-C26)	(C33-C34-C39-C41)	
3-t-Bu group	123.57	121.41	125.7	
	(C5-C3-C7-C9)	(C19-C18-C21-C23)	(C33-C32-C35-C37)	
	3.95	1.53	6.05	
	(C5-C3-C7-C10)	(C19-C18-C21-C24)	(C33-C32-C35-C38)	
	-115.50	-117.63	-112.10	
	(C5-C3-C7-C8)	(C19-C18-C21-C22)	(C33-C32-C35-C36)	

**Table 2.** Intramolecular hydrogen bonds and molecular conformations for enol-(*S*)-1 crystals.

In the  $\alpha$ -form crystal, four A molecules (yellow) exist in a unit cell (Figure 4a), and a pair of A molecules is arranged in a two-fold helical manner along all axes (Figure 4a–c) to form a herringbone structure along the *a*-axis (Figure 4c). In the  $\beta$ -form crystal, two B molecules (light pink) and two C molecules (light blue) coexist in a unit cell, and two pairs of B and C molecules are arranged in a two-fold helical manner along the *b*-axis (Figure 4d). The B and C molecules are arranged alternately along the *a*-axis to form a pseudo-herringbone structure (Figure 4f).



**Figure 4.** Crystal shape and molecular packings of the (**a**–**c**)  $\alpha$ -form and (**d**–**f**)  $\beta$ -form: (**a**,**d**) (010), (**b**,**e**) (100), and (**c**,**f**) (001) faces. The disordered 5-*tert*-butyl groups in minor occupancies and all hydrogen atoms are omitted for clarity.

We discuss a possible mechanism for the reversible SCSC phase transition, based on the changes in the molecular conformation and packing arrangement on the (001) face of the  $\alpha$ - and  $\beta$ -form crystals (Figure 5). The 5-*tert*-butyl groups of the A molecules of the right column rotate by approximately 60° (red circular arrow, Figure 5a) at the phase transition point  $T_c \approx 3$  °C under cooling; consequently, the A molecules of the right column change into C molecules (Figure 5b). However, the A molecules of the left column do not rotate at  $T_c$  under cooling; consequently, the A molecules of the left column change into B molecules (Figure 5b). Hence, two crystallographically independent molecules (B and C) are generated by these asymmetrical conformation changes in a pair of A molecules.

As described above, the dihedral angle  $41.6^{\circ}$  between the phenyl and salicyl planes in molecule A increases slightly to  $46.82^{\circ}$  and  $43.97^{\circ}$  in molecules B and C, respectively. Accordingly, the salicyl rings of the A molecules rotate slightly so that they are almost perpendicular to the (001) face (light blue circular arrow, Figure 5a). The dihedral angle between the salicyl plane and the (001) face increases from  $80.94^{\circ}$  (A) to  $85.90^{\circ}$  (B) and  $81.39^{\circ}$  (C). These conformation changes from A to B and C cause the loss of helical axes along the *a*- and *c*-axes, which induces the reordering of the packing arrangement from the orthorhombic space group  $P2_12_12_1$  ( $\alpha$ -form) to the monoclinic space group  $P2_1$  ( $\beta$ -form).



**Figure 5.** Molecular arrangements with the intermolecular interactions on the (001) face of the (**a**)  $\alpha$ - and (**b**)  $\beta$ -form crystals. The A molecules of the **left** column are converted into the B molecules after the phase transition. The A molecules of the **right** column are converted into the C molecules. The disordered 5-*tert*-butyl groups in minor occupancies are omitted for clarity.

The rotation of the salicyl rings toward the perpendicular to the (001) face leads to closer packing in the direction along the *a*-axis. As a result, the length of the *a*-axis shrinks discontinuously from 6.3058 to 6.2065 Å at the transition point,  $T_c$ . Before the phase transition, a weak intermolecular CH– $\pi$ interaction forms between the Schiff base and the phenyl plane of the A molecules in the *α*-form; the distance is 2.881 Å (black dotted line, Figures 5a and 6a). After the phase transition to the *β*-form, the distances of the CH– $\pi$  interactions between the B and C molecules shorten to 2.823 and 2.846 Å, respectively (Figures 5b and 6b). However, the changes in molecular conformation and the reordering of the packing arrangement are very small, which leads to the reversible SCSC phase transition with no destruction of the crystal lattice.



**Figure 6.** CH $-\pi$  interaction in the (**a**)  $\alpha$ -form and (**b**)  $\beta$ -form crystals.

The SCSC phase transition should lead to an anomalous change in the dielectric constant. Millimeter-size square plate  $\alpha$ -form crystals of enol-(*S*)-1 were obtained by slow evaporation of the 2-propanol solution at room temperature. The top surfaces were identified as the (010) and (0–10) faces by X-ray crystallography analysis. Hence, the dielectric constant of the depth direction along the *b*-axis was measured. A square plate crystal (5.4 × 4.8 × 0.7 mm long × wide × thick) was fabricated by coating the (010) and (0–10) top surfaces with a silver-based conductive paste, and enameled copper wires were attached to both top surfaces (Figure 7a,b). The temperature dependence of the real part of the dielectric constant  $\varepsilon_r$  was measured along the *b*-axis at 1 kHz (see the Experimental Section). The *T*– $\varepsilon_r$  curve revealed two step-like dielectric anomalies at around 3.4 and 3.9 °C upon cooling and then heating, respectively (Figure 7c), in agreement with the DSC results (Figure 1). These results also indicate that the transition is a first-order structural phase transition.



**Figure 7.** Square plate crystal of enol-(*S*)-**1** with application of silver paste and enameled copper wires: (**a**) the (010) top face and (**b**) the (001) side face (the scale bar is 1 mm); and (**c**) temperature dependence of dielectric constant for the enol-(*S*)-**1** crystal along the *b*-axis. The cooling scan was switched into the heating scan at 1.4 °C.

The dielectric constant  $\varepsilon_r$  increased from 2.636 to 2.671 (+1.33%) on cooling from 5.7 °C to 1.3 °C (Figure 7c). From the temperature dependence of the lattice constants in Figure 2, the surface area of the (010) face should decrease (-0.83%) and the thickness along the *b*-axis should also decrease (-0.09%) in the phase transition from the  $\alpha$ -form  $(10 \,^{\circ}\text{C})$  to the  $\beta$ -form  $(0 \,^{\circ}\text{C})$ . The calculated change in the dielectric constant caused by the slight decreases in surface area and depth is +0.74% from Equation (1), indicating a slight increase. Hence, the estimated real change in the dielectric constant corrected with the crystal volume shrinkage is +0.59% (=1.33% -0.74%) from Equation (1). This small change in the dielectric constant at the phase transition is derived from the small changes in the molecular conformation and packing arrangement between the  $\alpha$ - and  $\beta$ -form crystals. The maximum  $\varepsilon_{\rm r}$  value (2.67) of the  $\beta$ -form crystal of enol-(S)-1 along the *b*-axis at 1.5 °C is similar to that (2.7) of benzyl at  $-189 \,^{\circ}$ C [17] but is lower than those reported for ferroelectric organic crystals [1]. As shown in the packing diagrams (Figures 4 and 5), the intermolecular interactions in both the  $\alpha$ - and the  $\beta$ -form crystals are the van der Waals force and CH– $\pi$  interactions alone. Such weak intermolecular interactions might have induced the small dielectric constant  $\varepsilon_r$ . In fact, a large  $\varepsilon_r$  value (11) at room temperature has been reported for the croconic acid crystal, in which strong hydrogen-bonded sheets are formed [18].

#### 3. Experimental Section

#### 3.1. Materials

The compound enol-(*S*)-**1** was synthesized according to the literature procedure [14]. Single crystals were obtained by slow evaporation of the solution in 2-propanol at room temperature within several days. For X-ray crystallographic analysis and dielectric measurements, several single crystals were put into paraffin oil to wash them and were dried. Remaining crystals were used for DSC.

#### 3.2. Differential Scanning Calorimetry

DSC runs of enol-(*S*)-1 crystals (6.58 mg) were recorded using a DSC8500 (PerkinElmer, Norwalk, CT, USA) in the temperature range from 10 °C to -10 °C with a rate of 2 °C·min<sup>-1</sup> on cooling and heating under nitrogen at atmospheric pressure in aluminum crucibles with covers.

#### 3.3. Crystallography

α-form: Single-crystal X-ray diffraction data were collected at 10 °C with R-AXIS RAPID II (Rigaku, Tokyo, Japan) using Cu Kα radiation ( $\lambda$  = 1.54186 Å). The integrated and scaled data were empirically corrected for absorption effects with ABSCOR (Rigaku, Tokyo, Japan) [19]. The initial structures were solved by direct methods with SHELXT 2014 (Göttingen, Germany) [20] and refined on F<sub>0</sub><sup>2</sup> with SHELXL 2016 (Göttingen, Germany) [21]. With the exception of the disordered C atoms of the *tert*-butyl group in minor occupancies, the non-H atoms were refined anisotropically, and all of the H atoms were obtained geometrically and included in the calculations using the riding atom model.

β-form: Single-crystal X-ray diffraction data were collected at -50 °C with R-AXIS RAPID II (Rigaku) using Cu Kα radiation (λ = 1.54186 Å). The integrated and scaled data were empirically corrected for absorption effects with NUMABS (Rigaku, Tokyo, Japan) [22]. The initial structures were solved by direct methods with SHELXS 97 (Göttingen, Germany) [23] and refined on  $F_0^2$  with SHELXL 97 (Göttingen, Germany) [23]. With the exception of the disordered tertiary C atoms of the *tert*-butyl group, the non-H atoms were refined anisotropically, and all of the H atoms were obtained geometrically and included in the calculations using the riding atom model.

#### 3.4. Dielectric Measurements

The dielectric constant  $\varepsilon_r$  is defined by the equation below:

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A},\tag{1}$$

where *C* is the capacitance, in farads; *A* is the area of a crystal surface, in square meters;  $\varepsilon_0$  is the electric constant ( $\varepsilon_0 \approx 8.854 \times 10^{-12} \text{ Fm}^{-1}$ ); and *d* is the thickness of plate crystal, in meters. The square plate crystal was fabricated by application of silver-based conductive paste on the (010) and (0–10) top surfaces. The (010) area and the thickness of the crystal were measured by a digital high-speed microscope (VHX-5000; Keyence, Itaska, IL, USA). Capacitance was measured using with a capacitance bridge (1 kHz, AH 2550A; Andeen-Hagerling, Solon, OH, USA).

# 4. Conclusions

The chiral crystal of enantiomeric (*S*)-salicylidenephenylethylamine enol-(*S*)-1 undergoes a reversible SCSC phase transition at  $T_c \approx 3$  °C from the room temperature  $\alpha$ -form in orthorhombic space group  $P2_12_12_1$  to the low temperature  $\beta$ -form in monoclinic space group  $P2_1$  with a thermal hysteresis of around 1.7 °C. The most significant conformation change is the approximately 60° rotation of the 5-*tert*-butyl group of one molecule in the asymmetric unit of the  $\beta$ -form. The small changes in the molecular conformation and packing arrangement lead to the reversible SCSC transformation with no destruction of the crystal lattice. The dielectric constant along the *b*-axis is small, probably due to the weak intermolecular interactions.

**Supplementary Materials:** Supporting results (DSC and XRD) and CIF files (CCDC 1518678, 1518679) are available online at www.mdpi.com/2073-4352/7/1/7/s1. Figure S1: DSC curves of the enol-(*S*)-1 crystal over the temperature range from (a) -50 to +50 °C and (b) -10 to +110 °C on initial heating and then cooling; Figure S2: X-ray diffraction (XRD) patterns of the enol-(*S*)-1 crystal: powder XRD pattern measured at room temperature (black line) and calculated XRD pattern from the single crystal structure of the  $\alpha$ -form (red line).

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**Author Contributions:** Collection and assembly of data were conducted by Akifumi Takanabe. The draft of the paper was written by Akifumi Takanabe and Hideko Koshima. Takuro Katsufuji supported the dielectric constant measurement. The crystal structures were analyzed by Motoo Shiro, Kohei Johmoto, and Hidehiro Uekusa. Interpretation of data was conducted by Akifumi Takanabe, Hideko Koshima, and Toru Asahi. All authors have given approval to the final version of the paper.

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