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# Thermochromism of a novel organic compound in the solid state via crystal-to-crystal transformation

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#### Abstract

A novel thermochromic organic compound, 1,5-bis(hydroxyethylamino)-2,4-dinitrobenzene (BDB), was synthesized and characterized using X-ray diffraction, differential scanning calorimetry, visible and infrared spectroscopy. It was observed that BDB exists in two different crystal structures of A- and B-forms at room temperature. In each crystal structure, there exist intra- and intermolecular hydrogen bonds between hydroxy, amino, and nitro groups. As the temperature is increased, the color of BDB crystalline powder changes from yellow to orange. The yellow color was recovered for a specific period of time when it is cooled again, indicating that thermochromism of BDB in the solid state is reversible. Both crystals of A- and B-forms are transformed to the C-form crystal at the transition temperature. From the results of X-ray diffraction, thermal data, and infrared spectra, it is suggested that the thermochromism of BDB originates from the crystal-to-crystal transition accompanying with the configurational transformation between nitro-form and acidform via intramolecular hydrogen transfer.

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# 1. Introduction

Many organic compounds exhibit the change of color reversibly or irreversibly with temperature variation, socalled thermochromism [1,2]. Those compounds are of increasing importance in various practical applications such as temperature-indicating devices, temperature sensitive light filters, optical switching, imaging systems, etc. [1,3,4]. The most well-known thermochromic organic compounds are spiroheterocyclic compounds [5–10], Schiff bases [11–21], and overcrowded ethylenes [22–24].

Extensive studies on these compounds have revealed that the thermochromic mechanism is an equilibrium pro-

cess between two molecular species. For example, the thermochromic mechanism of spiroheterocyclic compounds such as spiropyrans and spirooxazines has been identified to involve a thermally sensitive equilibrium between the spiroheterocyclic form and the quasi-planar open merocyanine-like structure formed by ring opening via the C-O bond breaking [1,2]. It has also been reported that the thermochromic mechanism of Schiff bases involves an intramolecular hydrogen transfer, producing enol-keto tautomeric species [15,17], where the presence of the *ortho*-hydroxy group is essential for the observation of thermochromism [14,16,20]. Another important factor for these compounds to exhibit the thermochromism is the molecular packing of these compounds, i.e., the thermochromism is restricted to planar molecular packing which enables the tautomeric equilibrium to shift toward the keto-form absorbing at longer wavelengths as the temperature increases [20,25].

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The thermochromism of overcrowded ethylenes in solution also arises from a thermal equilibrium between two distinct and interconvertible isomeric species of A and B [26], where the isomeric species of A has a severe repulsion between the two overcrowded moieties that can be avoided by taking a folded conformation. This feature has been confirmed by X-ray crystallographic investigation and dynamic NMR studies [22–24]. Among various proposed structures for the thermo-induced species of B, the twisted conformation has been supported by a variety of experimental and theoretical works [22–24,27].

Until now, most of studies still focus on these organic compounds, because very few new thermochromic molecular systems have been developed [28,29]. In this study, we introduce a novel thermochromic organic compound of 1,5-bis(hydroxyethylamino)-2,4-dinitrobenzene (BDB), whose chemical structure is shown in Fig. 1, and investigate its crystal structure and thermochromic behavior in the solid state using X-ray diffraction, differential scanning calorimetry, visible and infrared spectroscopy. From the experimental results, the most feasible thermochromic mechanism of BDB is proposed in terms of both physical and chemical structural changes.

# 2. Experimental

### 2.1. Preparation and characterization of material

BDB was synthesized via two steps in our laboratory. First, *m*-dichlorobenzene (50 g, 0.34 mol) was reacted with KNO<sub>3</sub> (70 g, 0.693 mol) in a solution of concentrated H<sub>2</sub>SO<sub>4</sub> (250 ml) at 120–135 °C for 1 h. The reaction product of 2,6-dichloro-3,5-dinitrobenzene was filtered, dissolved in boiling 95% ethanol (1000 ml), and recrystallized at 0 °C. In the second step, 2,6-dichloro-3,5-dinitrobenzene (20 g, 0.084 mol) in ethanol (250 ml) was added dropwise into ethanolamine (23 g, 0.377 mol) in ethanol solution (50 ml). The mixed solution was stirred for 4 h to complete the reaction between 2,6-dichloro-3,5dinitrobenzene and ethanolamine. The crude product of BDB was filtered and purified by recrystallization using ethanol or THF solution. It was found that BDB crystallizes with two crystallographically different crystal structures, i.e., A- and B-forms, depending on the solvent used for recrystallization. The single crystals for A- and B-forms are prepared from THF and ethanol solution, respectively. In this study, sample codes for single crystals prepared from THF and ethanol solution are denoted as Samples I and II, respectively. Undoubtedly, Sample I consists of



Fig. 1. Chemical structure of 1,5-bis(hydroxyethylamino)-2,4-dinitrobenzene (BDB).

purely A-form crystal at room temperature and Sample II does contain B-form crystal.

The chemical structure of BDB ( $C_{10}H_{14}N_6O_4$ , 286.25 g/ mol) synthesized was identified using <sup>1</sup>H NMR spectroscopy and elemental analysis. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  8.98 (s, 1H); 8.48 (t, 2H); 5.97 (s, 1H); 5.06 (t, 2H); 3.68 (q, 4H); 3.44 (q, 4H). Elemental analysis of BDB: calcd C, 41.96; H, 4.93; N, 19.57. Found: C, 41.92; H, 5.04; N, 19.53. Both NMR and elemental analysis confirmed that BDB was successfully synthesized.

#### 2.2. X-ray crystal structure determination

Single crystals of A- and B-forms suitable for X-ray crystallographic work were grown by slow evaporation of THF and ethanol solutions of BDB, respectively. Each crystal on a glass fiber was mounted on a Siemens SMART diffractometer equipped with a graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation source and a CCD area detector. Data collection were performed at 298(2) K. Crystal data and structure refinements for A- and B-forms of BDB are summarized in Table 1. The crystal structures were solved by a direct method with SHELXL [30], in which full-matrix least-squares on  $F^2$  was used for refinement including hydrogen atoms and isotropic displacement parameters. All non-hydrogen atoms were obtained from difference electron density maps, and refined isotropically.

Table	1
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Crystallographic data of BDB A- and B-form crystals

	A-form	B-form
Formula	C <sub>10</sub> H <sub>14</sub> N <sub>14</sub> O <sub>6</sub>	C10H14N14O6
Formula weight	286.25	286.25
Temperature (K)	298(2)	298(2)
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca	$P2_1/n$
a (Å)	17.4534(13)	10.4691(8)
<i>b</i> (Å)	7.0324(5)	9.4703(7)
<i>c</i> (Å)	19.3742(14)	12.5781(10)
α (°)	90	90
β (°)	90	102.525(2)
γ (°)	90	90
Volume ( $Å^3$ )	2378.0(3)	1217.38(16)
Z	8	4
Calculated density (g/cm <sup>3</sup> )	1.599	1.562
Absorption coefficient $(mm^{-1})$	0.134	0.130
F(000)	1200	600
Crystal size (mm)	$0.5 \times 0.4 \times 0.4$	$0.5 \times 0.5 \times 0.4$
$\theta$ range for data collection (°)	2.10-26.37	2.30-26.37
Reflections collected	12,814	6886
Independent reflections	2428 ( $R_{\rm int} = 0.0305$ )	2483
		$(R_{\rm int} = 0.0280)$
Data/restraints/parameters	2428/0/238	2483/0/272
Goodness-of-fit on $F^2$	1.027	1.031
Final <i>R</i> indices $[I \ge 2 \sigma(I)]$	R1 = 0.0318	R1 = 0.0415
	wR2 = 0.0830	wR2 = 0.1052
R indices (all data)	R1 = 0.0411	R1 = 0.0576
	wR2 = 0.0886	wR2 = 0.1142
Largest differences peak and hole (e $Å^{-3}$ )	0.218 and -0.152	0.210 and -0.331

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#### 2.3. Characterization of thermochromic behavior

Temperature-dependent X-ray powder diffractograms of Samples I and II were obtained using a wide-angle X-ray diffractometer (GADDS, Bruker) equipped with a general area detector and heating accessary.

Thermal properties of BDB crystals were measured with a Perkin-Elmer DSC Pyris-1 equipped with an intercooler system. Temperature and heat flow were calibrated using the high-purity indium standard (156.6 °C and 28.45 J/g). Heating and cooling rates were 2 or 10 °C/min.

For BDB crystalline film cast on a glass plate, visible spectra were obtained as a function of temperature or time using a UV/vis reflectance spectrophotometer (ColorEye 3100, Gretag Macbeth, USA). Infrared spectra of BDB crystal powder in KBr pellet were obtained using a Per-kin-Elmer 2000 FT-IR spectrometer equipped with a custom-designed temperature-controlling accessory. Each infrared spectrum at different temperature was obtained by averaging 128 scans with the resolution of 2 cm<sup>-1</sup>.

# 3. Results and discussion

# 3.1. Molecular and crystal structures

Crystal structures of BDB A- and B-forms were identified using single-crystal X-ray crystallography. Their bond

Table 2 Bond lengths (Å) and angles (°) in A- and B-form crystals

lengths and angles are listed in Table 2. Molecular structures and perspective packing views of A- and B-forms are also shown in Figs. 2 and 3, respectively. Both molecular structures exhibit intramolecular hydrogen bonding interactions between nitro-oxygen atoms and adjacent amino-protons. The A-form shows another intramolecular hydrogen bonding interaction arising from two hydroxyl groups of amino-alcohol chains. To the contrary, similar hydrogen bonding is not found in the *B*-form. The crystal structure of A-form also reveals that flexible amino-alcohol chains are well ordered due to the intermolecular non-classical hydrogen bonding interactions [31] between hydrogen atoms attached C8 and C10 and the nitro-oxygen atoms in neighbors, as well as intramolecular hydrogen bonding interactions between two hydroxyl groups of amino-alcohol chains. On the other hand, one of flexible amino-alcohol chains with C9 and C10 in the B-form crystal is disordered into the two positions, as shown in Fig. 3a. The relative probability of atomic positions of N4-C9-C10-O6 and N4-C9'-C10'-O6 in the B-form crystal was estimated to be 0.64-0.36, respectively. In both A- and Bform crystals, all the nitro and amino groups except hydroxyl ethyl chains are nearly coplanar with the benzene ring as can be seen in Figs. 2a and 3a, resulting in facile intra-hydrogen bonding interactions. The hydroxy ethyl groups in the A-form have different torsional angles from those in the B-form, leading to the different molecular

Bond length (Å)			Bond angle (°)		
Bond	A-form	<i>B</i> -form	Bond	A-form	<i>B</i> -form
01-N1	1.2375(16)	1.2364(18)	O2-N1-O1	121.52(12)	121.49(15)
O2-N1	1.2307(15)	1.2220(19)	O2-N1-C1	119.30(12)	119.03(14)
O3–N2	1.2265(16)	1.2318(18)	O1-N1-C1	119.18(11)	119.48(13)
O4–N2	1.2356(15)	1.239(2)	O3-N2-O4	121.17(11)	121.74(14)
O5–C8	1.416(2)	1.424(2)	O3-N2-C5	119.52(11)	119.19(15)
O6-C10	1.4268(18)	1.547(6)	O4-N2-C5	119.30(11)	119.06(14)
O6-C10'	_	1.457(6)	C2-N3-C7	125.06(12)	123.27(15)
N1-C1	1.4335(17)	1.437(2)	C4-N4-C9	125.64(12)	123.54(19)
N2-C5	1.4312(17)	1.437(2)	C4-N4-C9'	_	115.5(3)
N3-C2	1.3491(17)	1.340(2)	C6-C1-C2	120.41(11)	120.51(14)
N3-C7	1.4542(19)	1.452(2)	C6-C1-N1	116.74(12)	117.00(14)
N4C4	1.3465(17)	1.346(2)	N1-C1-C2	122.84(11)	122.45(14)
N4-C9	1.4581(17)	1.461(4)	N3-C2-C3	121.09(12)	120.13(15)
N4-C9′	_	1.639(8)	N3-C2-C1	122.57(12)	123.52(14)
C1-C6	1.3757(18)	1.377(2)	C3-C2-C1	116.34(11)	116.35(14)
C1–C2	1.4397(19)	1.431(2)	C2-C3-C4	124.92(12)	124.70(16)
C2–C3	1.3936(18)	1.396(2)	N4-C4-C3	121.17(12)	120.64(16)
C3–C4	1.3985(18)	1.393(2)	N4-C4-C5	122.81(12)	123.14(16)
C4–C5	1.4416(18)	1.434(2)	C3-C4-C5	116.02(11)	116.21(15)
C5–C6	1.3798(18)	1.378(2)	C6-C5-N2	116.29(12)	116.80(14)
C7–C8	1.525(2)	1.505(2)	C6-C5-C4	120.44(12)	120.56(14)
C9-C10	1.518(2)	1.516(6)	N2-C5-C4	123.26(11)	122.63(15)
C9'-C10'	_	1.505(10)	C1-C6-C5	121.83(12)	121.54(15)
			N3-C7-C8	116.05(14)	110.47(15)
			O5–C8–C7	115.50(14)	111.87(16)
			N4-C9-C10	114.16(12)	104.7(3)
			O6-C10-C9	113.96(12)	104.0(3)
			O6-C10'-C9'	_	97.4(5)
			C10'-C9'-N4	_	103.6(5)



Fig. 2. (a) Molecular structure of the A-form with displacement ellipsoid of the 50% probability level. (b) Perspective packing view of the A-form down the crystallographic a axis. Hydrogen atoms are omitted for clarity in the packing diagram.

packing, when Fig. 2b is compared with 3b. Nonetheless, the molecular units are almost parallel to one another due to the aromatic  $\pi$ - $\pi$  interaction between benzene rings, regardless of crystalline forms. The inter-planar distances between benzene rings in the *A*-form are somewhat shorter than those in the *B*-form (Figs. 2b and 3b), resulting in the dense molecular packing in the *A*-form (Table 1). The dotted lines in Figs. 2 and 3 for asymmetric units and molecular packing of *A*- and *B*-forms indicate the intra- and intermolecular hydrogen bonding. Structural parameters for the intra- and intermolecular hydrogen bonds in *A*- and *B*-forms are summarized in Tables 3 and 4, respectively.

# 3.2. Thermochromic behavior

The BDB crystals exhibit optically yellow color at room temperature. This yellow color changes quickly to orange

when heated above 140 °C, regardless of the crystalline form of A or B. When the crystals are cooled down to room temperature, yellow color is recovered for a specific period of time, indicating that the thermochromism of BDB is reversible. It is noteworthy that this thermochromic behavior occurs in the solid state without melting. The visible spectrum of the thermochromic behavior was also obtained by measuring spectral reflectance (R) and by calculating color strength via the Kubelka-Munk equation  $[K/S = (1 - R)^2/2R]$ . When the K/S value (K, absorption coefficient; S, scattering coefficient) is plotted against wavelength, as shown in Fig. 4, it is realized that the absorption band at 480 nm is dominant below 140 °C and that the band at 500 nm becomes predominant above 140 °C (Fig. 4a). This spectral shift from 480 to 500 nm with temperature (bathochromic or red shift) corresponds to the change of color from yellow to orange in the solid state. When the heated crystalline film is cooled to room



Fig. 3. (a) Molecular structure of the B-form with displacement ellipsoid of the 50% probability level. (b) Perspective packing view of the B-form down the crystallographic b axis. Hydrogen atoms and disordered part are omitted for clarity in the packing diagram.

Table 3
Intra- and intermolecular hydrogen bonding geometry in A-form crystal

D-H··· $A$	D-H	$\mathbf{H} \cdots \mathbf{A}$	$D \cdots A$	D-H··· $A$
O6–H6· · · O5	0.84(2)	1.98(2)	2.812(2)	175(2)
N3–H3···O1	0.85(2)	2.06(2)	2.691(2)	131(1)
N4–H4···O4	0.86(2)	2.02(2)	2.665(2)	131(2)
$C8-H8A\cdots O2^{(1)}$	0.97(2)	2.55(2)	3.384(2)	145(2)
C10–H10B· $\cdot \cdot O3^{(1)}$	0.98(2)	2.59(2)	3.391(2)	138(1)
$O5H5\cdots O6^{(2)}$	0.82(2)	1.93(3)	2.753(2)	175(2)

Symmetry codes: (1) x, 0.5 - y, 0.5 + z - 1; (2) 1 - x, 0.5 + y, 0.5 - z.

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Table 4						
Intra- and intermolecular	hydrogen	bonding	geometry	in	B-form	crystal

			•	•
D-H···A	D-H	$H \cdots A$	$D \cdots A$	D-H··· $A$
N3–H3· · ·O1	0.85(2)	1.95(2)	2.644(2)	137(2)
N4–H4···O4	0.82(2)	1.98(2)	2.637(2)	136(2)
$O5-H5\cdots O6^{(1)}$	0.87(3)	2.05(3)	2.893(2)	162(3)
$O6-H6\cdots O5^{(2)}$	0.85(3)	1.90(3)	2.746(2)	170(2)
$C8^{(3)}-H8A^{(3)}\cdots O4$	0.97(2)	2.52(2)	3.414(2)	154(2)
$C8^{(4)}$ -H8 $A^{(4)}$ ···O2	0.97(2)	2.57(2)	3.142(2)	118(1)

Symmetry codes: (1) 0.5 - x, 0.5 + y - 1, 0.5 - z + 1; (2) x, y + 1, z; (3) 0.5 + x, 0.5 - y + 1, 0.5 + z - 1; (4) 0.5 + x, 0.5 - y, 0.5 + z - 1.





Fig. 4. Visible spectra of BDB crystalline films: (a) temperature-dependent spectra; (b) time-dependent spectra. The optical images in (a) were taken at 25 and 160 °C. The spectra in (b) were obtained at 25 °C after cooling from 160 °C.

temperature, the original visible spectrum at room temperature was recovered for a period of time, as shown in Fig. 4b.

In order to investigate the change of crystal structure at the thermochromic transition, X-ray diffractograms of Samples I and II were obtained as a function of temperature, as shown in Fig. 5. X-ray diffractograms of both samples exhibit sharp crystalline diffraction peaks before and after the thermochromic transition. It is noticeable that the X-ray diffractogram of Sample I is identical with that of Sample II above the thermochromic transition temperature. These results lead us to conclude that the thermochromism of BDB occurs via the crystal-to-crystal transition and that the crystals of A- and B-forms are transformed to an identical crystal designated as the C-form hereafter. Here it should be noted that it is not possible to identify the crystal structure of C-form developed above the thermochromic transition temperature by the X-ray diffraction method used in this study, because it is very difficult to obtain a single crystal of the C-form. The molecular and crystalline structure of C-form is under investigation using

Fig. 5. X-ray powder diffractograms of Samples I and II at 25 and 150 °C.

the molecular modelling and the quantum mechanical calculation based on the density functional theory, and will be reported in future.

The thermochromic transition behavior of BDB crystals is also characterized by differential scanning calorimetry (DSC). Fig. 6 shows the DSC heating and cooling thermograms of Samples I and II. The heating thermograms show two endothermic peaks at 127 and 211 °C for Sample I and at 140 and 211 °C for Sample II. Integrating all the data of visible spectra, DSC and X-ray diffraction leads us to conclude that the endothermic peaks at 127 °C for Sample I and at 140 °C for Sample II are attributed to the crystalto-crystal transition (from A- or B-form to C-form) for the thermochromism and the peak at 211 °C corresponds to the melting point of the C-form crystal transformed from A- or B-form crystal. It is believed that the different crystal-to-crystal transition temperatures  $(T_{cc})$  and enthalpies  $(\Delta H_{cc}^{o})$  of Samples I and II originate from different molecular packing in A- and B-forms. On the other hand, the almost same melting temperature  $(T_{\rm m} \sim 211 \text{ °C})$  and enthalpy ( $\Delta H_{\rm m}^{\rm o} \sim 5.8$  kcal/mol) of the crystals transformed from Samples I and II indicate that the C-form crystals transformed from the A- or B-form are identical, which is exactly consistent with the X-ray diffraction results. Since



Fig. 6. DSC heating and cooling thermograms for Samples I and II at the heating and cooling rates of 2  $^{\circ}\mathrm{C/min}.$ 

the cooling thermograms in Fig. 6 show only one exothermic peak at around 200 °C, it is assumed that the exothermic peak corresponds to the crystallization from the melt to the C-form crystal. Indeed, the second heating thermogram of the just-cooled sample shows an endothermic melting peak at 211 °C, which corresponds to the melting of the C-form crystal, as shown in Fig. 7a. As the holding time at -15 °C increases, two endothermic peaks at 127 and 140 °C appear and their intensities increase, as can be seen in Figs. 7b–g. It reveals that the C-form crystal transforms to the A- and/or B-form for the period of time at the holding temperature. Therefore, it is concluded that the two endothermic peaks at 127 and 140 °C in Fig. 7 arise from the transformation of A- and B-form crystals regenerated at the holding temperature to the C-form. In addition, it is realized from the relative area of endothermic peaks at 127 and 140 °C that the transformation from the C-form to the A-form crystal is larger than the transformation from the C-form to the B-form crystal.

Now one may have a question whether or not any configurational change of BDB occurs during the thermochromic transition. The answer might not be clearly unravelled until the crystal structure of *C*-form is fully identified. Since



Fig. 7. DSC heating curves at the heating rate of 10 °C/min. The sample was first kept at 160 °C for 3 min, cooled to -15 °C, and maintained for a specified period of time: (a) 1 h; (b) 3 h; (c) 16 h; (d) 24 h; (e) 48 h; (f) 73 h; (g) 168 h.

the crystal structure of C-form could not be determined by the X-ray diffraction method as mentioned above, the temperature-dependent infrared spectroscopy is inevitably employed to investigate the configurational change during the thermochromic transition. Fig. 8 shows infrared spectra of Samples I and II at 25 and 150 °C. Close examination of Fig. 8 reveals that the infrared spectra of Samples I and II at 25 °C are slightly different from each other, since the molecular conformation and the crystal packing of A-form are different from those of *B*-form. On the other hand, the spectra of Samples I and II at 150 °C are nearly identical, indicating that the crystal structures of Samples I and II above  $T_{cc}$  are identical, which is in agreement with the results from X-ray diffraction and thermal analysis. Table 5 summarizes the assignment of infrared bands of BDB crystals below and above  $T_{cc}$ , which may provide some information on the configurational change at the thermochromic transition. First, two NH stretching bands at 3388 and  $3346 \text{ cm}^{-1}$  for Samples I and at 3388 and 3367 cm<sup>-1</sup> for Sample II below  $T_{cc}$  are merged into a single broader band of 3365 cm<sup>-1</sup> above  $T_{cc}$ . Here two sharp NH stretching bands of respective A- and B-forms indicate that two hydroxyl ethyl groups have different conformations. Second, the intensity of C=C stretching band of benzene ring at 1620 cm<sup>-1</sup> decreases significantly above  $T_{cc}$ , while a new strong C=N stretching band at  $1642 \text{ cm}^{-1}$  appears. Third, the intensity of the  $NO_2$  stretching bands at 1545, 1480, and 1347 cm<sup>-1</sup> becomes much weaker above  $T_{cc}$ . Finally, a new band at  $3550 \text{ cm}^{-1}$  appears, as the temperature increases from 25 to 150 °C. The new band at  $3550 \text{ cm}^{-1}$  is believed to arise from the OH stretching of



Fig. 8. FT-IR spectra of Samples I and II at 25 and 150 °C.

Table 5

Assignment of characteristic infrared bands of BDB crystals below and above the thermochromic transition temperature

Wavenumber (cm <sup>-1</sup> )	Assignment	Crystalline form
3550	v(OH) from = N–OH	С
3388, 3367, 3346	v(NH)	A and/or B
3365	v(NH)	С
3260	v(OH)	A, B, and C
1642	v(C-N)	С
1620	v(C-C)	A, B, and C
1545	$v(NO_2)$	A, B, and C
1480	$v(C-C), v(NO_2)$	A, B, and C
1347	$v(NO_2)$	A, B, and C

newly formed N-OH groups. Based on the change of characteristic infrared bands, it is speculated that the conformation of BDB crystal changes from a nitro-form below  $T_{cc}$  to an acid-form above  $T_{cc}$ , as schematically shown in Fig. 9. As described above, there exist intra- and intermolecular hydrogen bonds between hydroxyl, amino, and nitro groups in each crystal structure of A- and B-forms below  $T_{\rm cc}$ . However, the intramolecular distance between amine proton and the oxygen atom of the nitro group is closer than any other intermolecular distances for both A- and B-form crystals, as listed in Tables 3 and 4. Therefore, it is expected that the intramolecular hydrogen transfer from the amine proton to the nitro-oxygen takes place dominantly during the thermochromic transition, leading to the configurational transformation from nitro-form to acid-form. This thermochromic mechanism of BDB seems to be quite similar to the one of Schiff-bases, which occurs in the solid state through the configurational transformation between two equilibrium species via hydrogen transfer. In short, it is valid to conclude from the results of X-ray diffraction, DSC, and infrared spectra that the first order crystal-to-crystal transition of BDB occurs simultaneously with configurational transformation at the solid-state thermochromic transition.

# 4. Conclusions

A novel organic crystal of 1,5-bis(hydroxyethylamino) -2,4-dinitrobenzene (BDB) was prepared, and its thermochromic mechanism was investigated using X-ray diffraction, DSC, visible and infrared spectroscopy. BDB crystals were developed into two different crystal structures (A- and B-forms) at room temperature, depending on the solvent used for recrystallization. Both A- and B-form crystalline powders exhibited reversible change of color from vellow to orange in the solid state. The thermochromic transition temperatures, which correspond to the crystal-to-crystal transition temperatures, were determined to be 127 °C for A-form and 140 °C for B-form. It was found that both crystals of A- and B-forms were transformed to the C-form crystal at the thermochromic transition. Comparison of the infrared spectra before and after the thermochromic transition revealed that the configurational transformation between nitro-form and acid-form via intramolecular hydrogen



Nitro-form (below  $T_{cc}$ )

Acid-form (above  $T_{cc}$ )

transfer occurs at the thermochromic transition. Therefore, it is suggested that the thermochromic transition of BDB in the solid state arises from the crystal-to-crystal transition accompanying with the configurational transformation.

# 5. Supporting information available

CCDC 289537 and 289538 contain the supplementary crystallographic data for BDB *A*- and *B*-forms in CIF format, respectively. 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 336033).

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc. 2006.04.025.

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