Electronic Supplementary Information for

A Thermo-Responsive Structural Switch and Colossal Anisotropic Thermal Expansion in a Chiral Organic Solid

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1. Synthesis of Trianglimine.

Trianglimine (**TI**) was synthesised in the Organic Stereochemistry Group at Adam Mickiewicz University in Poznan according to the method published by Gawronski et al.[1] Purification was achieved by crystallisation from ethyl acetate.

2. Single crystal X-ray diffraction

Crystals of Forms I and II suitable for single-crystal X-ray diffraction were obtained from the slow evaporation of a mixture dichloromethane and acetonitrile (Form I) and acetone (Form II). Reflection intensities for Form I were measured on a SuperNova diffractometer equipped with a Cu microfocus source (λ =1.54178 Å) and a 135 mm Atlas CCD detector. The sample temperature (form 295 to 130 K) was controlled with an Oxford Instruments Cryosystem cold nitrogen-gas blower. Data reduction and analysis for this crystal was carried out with the CrysAlisPro program.[2] The data for Form II were collected on a Bruker Apex II DUO CCD diffractometer equipped with a multilayer monochromator and CuK α radiation (λ = 1.54178 Å). The temperature of the crystal (from 400 to 100 K) was controlled using an Oxford Cryostream 700 Plus. Data reduction was carried out by means of a standard procedure using the Bruker software package SAINT.[3] The absorption correction for Form II at 295K was based on multiple and symmetry equivalent reflections in the data set by using the SADABS program.[4]

The structures of both Forms I and II were solved by direct methods using the SHELXS-97[5] program and were refined by full matrix least squares on F^2 using the program SHELXL-2015[6] through the graphical interface X-Seed.[7]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms bound to C atoms were placed at calculated positions and refined using a riding model, and their isotropic displacement parameters were given a value 20% higher than the isotropic equivalent for the atom to which the H atoms were attached. The absolute structure of the investigated crystals was assumed from the known absolute configuration of the (*R*,*R*)-1,2-diaminecyclohexane which was used as a starting material in the syntheses. The relevant crystal data collection and refinement parameters are listed in Tables S1 and S2. X-Seed[7] and Mercury[8] were used for preparing figures.

	Form I_295K	Form I_130K
Temperature (K)	295	130
<i>a</i> , <i>b</i> , <i>c</i> (Å)	31.3940 (9), 5.3361 (2), 23.9306 (7)	31.2568 (10), 5.2632 (2), 23.9083 (8)
β (°)	100.532 (3)	100.653 (3)
$V(Å^3)$	3941.4 (2)	3865.4 (2)

Table S1. Crystal data, data collection and refinement parameters for Form I.

μ (mm ⁻¹)	0.49	0.50
Crystal size (mm)	$0.48 \times 0.16 \times 0.06$	$0.48 \times 0.16 \times 0.06$
T_{\min}, T_{\max}	0.691, 1.000	0.806, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	17515, 7597, 6259	17619, 7553, 7068
R _{int}	0.024	0.033
$(\sin \theta / \lambda)_{max} (\text{Å}^{-1})$	0.628	0.629
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.045, 0.133, 1.03	0.047, 0.136, 1.05
No. of reflections	7597	7553
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} ({ m e}{ m \AA}^{-3})$	0.11, -0.13	0.17, -0.22
Absolute structure parameter	0.2 (3)	0.0 (3)

 Table S2. Crystal data, data collection and refinement parameters for Form II and III.

	Form II_400K	Form II_295K	Form III_100K
Temperature (K)	400	295	100
a, b, c (Å)	34.6765 (8), 5.3631(2), 22.8467 (5)	34.7168 (4), 5.2783 (1), 22.8445 (3)	32.4316 (17), 5.1870(3), 22.8480 (12)
β (°)	112.324 (1)	112.593 (1)	104.905 (4)
$V(Å^3)$	3930.43 (19)	3864.90 (10)	3714.2 (4)
μ (mm ⁻¹)	0.49	0.50	0.52
Crystal size (mm)	$0.30 \times 0.12 \times 0.08$	$0.30 \times 0.12 \times 0.08$	$0.30 \times 0.12 \times 0.08$
Absorption correction	None	Multi-scan SADABS 2008/1 (Bruker AXS, 2008)	none
T_{\min}, T_{\max}	-	0.660, 0.753	_
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	11634, 5965, 4705	33746, 6562, 6066	22421, 6438, 4495
R _{int}	0.027	0.035	0.090
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.594	0.595	0.613
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.055, 0.166, 1.04	0.037, 0.102, 1.03	0.054, 0.132, 0.96
No. of reflections	5965	6562	6438
No. of parameters	434	433	434
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} ({\rm e}~{\rm \AA}^{-3})$	0.12, -0.10	0.09, -0.17	0.22, -0.22
Absolute structure parameter	-0.1 (8)	-0.1 (2)	0.0 (7)



Figure S1. (a) Labelling scheme used for the asymmetric units of all crystal structures determined at different temperatures. b) view of the molecular overlap of both Forms II (red) and III (blue) at 295 and 100 K, respectively; c) for comparison, view of the molecular overlap of Forms I (green) and II (red), which were obtained by crystallization from different solvents.



Figure S2. Comparison of the calculated powder patterns of polymorphic forms of TI.

3. Variable temperature single-crystal X-ray diffraction

Variable temperature single-crystal X-ray diffraction experiments were carried out on crystals of Forms I and II, which were glued to a thin glass fiber and enveloped in a temperature-controlled stream of dry nitrogen gas during data collection, in each case. Unit cell parameters were monitored at intervals of 15 K from 295 to 130 K for Form I, and from 400 to 100 K for Form II. The interval was reduced close to the temperature of the phase transition of Form II.

Table S3. Form I lattice parameter values determined from variable temperature X-ray diffraction experiments on cooling and heating over the temperature ranges $295 \rightarrow 130 \rightarrow 295$ K.

T (°)	a [Å]	<i>b</i> [Å]	<i>c</i> [Å]	β(°)	V[Å ³]
295	31.300(18)	5.310(5)	23.925(15)	100.57(5)	3934(5)
280	31.290(20)	5.309(7)	23.929(18)	100.59(6)	3917(7)
265	31.292(20)	5.308(7)	23.925(18)	100.66(7)	3910(7)
250	31.280(20)	5.307(6)	23.934(17)	100.60(6)	3908(6)
235	31.281(20)	5.306(6)	23.914(17)	100.55(6)	3901(6)
220	31.291(15)	5.304(5)	23.919(13)	100.54(4)	3902(5)
205	31.289(16)	5.295(7)	23.908(12)	100.51(4)	3877(6)
190	31.260(20)	5.292(6)	23.914(16)	100.66(6)	3889(6)

175	31.251(20)	5.291(7)	23.905(15)	100.68(5)	3867(6)
160	31.244(14)	5.293(6)	23.903(14)	100.69(4)	3871(5)
145	31.252(2)	5.291(4)	23.910(16)	100.70(6)	3875(5)
130	31.240(19)	5.279(6)	23.937(14)	100.44(5)	3860(5)
145	31.245(15)	5.273(6)	23.890(13)	100.64(4)	3869(5)
160	31.251(16)	5.256(7)	23.892(11)	100.56(4)	3858(7)
175	31.261(19)	5.275(6)	23.915(15)	100.69(5)	3882(5)
190	31.272(16)	5.276(7)	23.894(11)	100.56(4)	3876(6)
205	31.261(20)	5.278(6)	23.877(16)	100.58(6)	3887(6)
220	31.270(20)	5.282(7)	23.891(16)	100.56(6)	3893(6)
235	31.280(20)	5.285(6)	23.904(17)	100.63(6)	3899(6)
250	31.300(2)	5.289(7)	23.903(17)	100.53(6)	3903(6)
265	31.290(20)	5.290(7)	23.895(18)	100.57(6)	3910(7)
280	31.311(20)	5.295(6)	23.900(17)	100.52(6)	3917(6)
295	31.300(18)	5.293(5)	23.925(15)	100.47(5)	3934(5)

Table S4. Lattice parameters of Forms II and III determined from variable temperature X-ray diffraction experiments on cooling and heating over the temperature ranges $400 \rightarrow 100 \rightarrow 400$ K.

T (°)	a [Å]	<i>b</i> [Å]	<i>c</i> [Å]	β(°)	V [ų]
400	34.665(7)	5.362(1)	22.811(1)	112.26(3)	3923.6(1)
385	34.677(7)	5.350(1)	22.813(1)	112.32(4)	3915.1(1)
370	34.682(8)	5.340(1)	22.809(1)	112.35(2)	3906.8(1)
355	34.687(7)	5.323(1)	22.816(1)	112.40(1)	3895.0(1)
340	34.685(7)	5.313(1)	22.808(1)	112.42(5)	3885.1(1)
325	34.688(7)	5.300(1)	22.808(1)	112.47(3)	3874.9(1)
310	34.699(7)	5.287(1)	22.817(1)	112.52(2)	3866.7(1)
295	34.704(7)	5.272(1)	22.807(1)	112.54(4)	3854.5(1)
280	34.706(9)	5.260(1)	22.804(1)	112.53(3)	3845.1(1)
265	34.707(7)	5.250(1)	22.804(1)	112.59(3)	3836.3(1)
250	34.710(14)	5.242(1)	22.801(1)	112.64(3)	3829.1(1)
235	34.715(8)	5.234(1)	22.795(1)	112.66(3)	3822.6(1)
226	34.724(6)	5.228(1)	22.806(2)	112.69(5)	3819.8(1)
225	32.524(12)	5.248(1)	22.903(1)	104.40(3)	3786.6(1)
220	32.509(4)	5.244(1)	22.900(1)	104.38(4)	3781.8(1)
205	32.504(7)	5.236(1)	22.899(2)	104.47(2)	3773.7(1)
190	32.499(11)	5.228(1)	22.898(2)	104.55(2)	3765.9(1)
175	32.497(10)	5.223(1)	22.884(2)	104.60(3)	3758.5(1)
160	32.490(12)	5.212(1)	22.88(2)	104.65(3)	3748.7(1)
145	32.477(15)	5.205(1)	22.875(2)	104.69(4)	3740.6(1)
130	32.461(12)	5.200(1)	22.867(2)	104.76(4)	3732.3(1)
115	32.459(13)	5.192(1)	22.854(2)	104.79(4)	3723.7(1)

100	32.451(13)	5.186(1)	22.840(2)	104.82(3)	3715.8(1)
115	32.457(11)	5.191(1)	22.872(2)	104.82(3)	3725.4(1)
130	32.468(11)	5.200(1)	22.862(2)	104.74(3)	3732.6(1)
145	32.472(10)	5.205(1)	22.864(2)	104.69(3)	3737.9(1)
160	32.477(12)	5.211(1)	22.878(2)	104.61(3)	3746.6(1)
175	32.496(13)	5.217(1)	22.887(1)	104.57(3)	3755.6(1)
190	32.502(11)	5.229(1)	22.885(1)	104.51(3)	3765.6(1)
205	32.509(9)	5.235(1)	22.898(1)	104.47(3)	3773.1(1)
220	32.514(9)	5.245(1)	22.901(1)	104.40(3)	3782.5(1)
235	32.525(6)	5.255(1)	22.909(1)	104.38(4)	3794.0(1)
248	32.531(11)	5.262(1)	22.906(1)	104.28(5)	3799.7(1)
249	34.717(8)	5.242(1)	22.808(1)	112.64(3)	3830.9(1)
250	34.717(5)	5.245(1)	22.806(1)	112.65(4)	3832.6(1)
265	34.714(9)	5.253(1)	22.813(2)	112.63(2)	3839.7(1)
280	34.709(6)	5.260(1)	22.814(1)	112.50(2)	3846.1(1)
295	34.704(8)	5.271(1)	22.806(1)	112.54(4)	3853.4(1)
310	34.701(9)	5.285(1)	22.814(1)	112.51(1)	3865.4(1)
325	34.694(12)	5.296(1)	22.817(1)	112.45(2)	3874.6(1)
340	34.694(9)	5.309(1)	22.812(2)	112.42(2)	3884.2(1)
355	34.691(8)	5.326(1)	22.810(1)	112.40(1)	3896.2(1)
370	34.673(9)	5.339(1)	22.808(2)	112.33(1)	3905.2(1)
385	34.665(10)	5.348(1)	22.808(2)	112.30(1)	3911.8(1)
400	34.665(11)	5.362(1)	22.811(2)	112.26(1)	3923.6(1)



Figure S3: Thermal variation of the unit cell parameters and unit cell volumes for Form **II** in the temperature range from 400 to 226 K and Form **III** in the range of 225 to 100 K, over which the same crystal was studied.



Figure S4: Thermal variation of the unit cell parameters and unit cell volumes for Form **III** in the temperature range from 100 to 248 K and Form **II** in the range of 249 to 400 K, over which the same crystal was studied.

4. Variable temperature powder X-ray diffraction (VT-PXRD)

VT-PXRD experiments were carried out for Form II on a PANalytical X'Pert PRO instrument with Bragg-Brentano geometry, and equipped with a CuK α source ($\lambda = 1.5418$ Å) and an X'Celerator detector. All measurements employed the θ/θ scan mode and intensities were recorded for 2 θ angles between 5 and 40°. The sample was sealed within a glass capillary and the capillary spinner configuration of the instrument was used since this setup allows for very accurate temperature control using an Oxford Cryostream 700Plus cryostat.



Figure S5. Variable temperature PXRD patterns of **Forms II** and **III** measured with the interval of 20 K on cooling-heating in the temperature range 293-133 K. The phase transition occurs between 213 and 193 K upon cooling, and between 233 and 253 K upon heating.

5. Differential scanning calorimetry (DSC).

DSC experiments were carried out using a TA Instruments Q100 calorimeter equipped with a Liquid Nitrogen Cooling Accessory (LNCS) or a Q20 calorimeter equipped with a Refrigerated Cooling System (RCS90). Phase I was cooled from 25 to -160 °C and subsequently heated to 160 °C and then cooled to 25 °C at a rate of 10 °C/min. Phase II was cooled down to -180 °C and subsequently heated to 150 °C and then cooled to 25 °C at a rate of 10 °C/min.



Figure S6: DSC thermograms of heating-cooling cycles for Form II.



Figure S7: For comparison DSC thermogram of heating–cooling cycles for Form **I**, which does not show any notable thermal events.

6. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out using a TA Instruments Q500 thermogravimetric analyser. The sample was heated at a constant heating rate of 10 °C/min from room temperature to 500 °C (Figure S7). The furnace was purged with N_2 gas flowing at a rate of 50 cm³ min⁻¹.



Figure S8: TGA thermograms for the two polymorphic Forms I (green) and II (red). Forms I and II decompose with an onset temperature of approximately 347 and 337 °C, respectively.

7. Hot-stage microscopy (HSM).

The experiment was carried out with Linkam hot stage system consisting of a THMS600 hot stage, a T95 System Controller and LNP95 liquid nitrogen cooling pump for cooling to -196 °C. Images were recorded using an Olympus SZX10 microscope equipped with a Watec analogue video camera. The crystal was cooled from 25 to -60 °C and subsequently heated to 25 °C at a rate of 5 °C/min.

8. PASCal

PASCal calculations [9] were carried out online at http://pascal.chem.ox.ac.uk using the finite strain option. The phase transformations were not taken into account when calculating the thermal expansion coefficients (α_i).

7.1. Form **I**

Axes	α (MK ⁻¹)	ασ (MK ⁻¹)	a	Ь	с
<i>X</i> ₁	6.4616	6.9826	0.2993	-0.0000	0.9541
<i>X</i> ₂	14.4118	1.2270	-0.9519	-0.0000	0.3063
<i>X</i> ₃	22.4423	2.1868	0.0000	-1.0000	-0.0000
V	50.9316	5.6601			

Table S5. Principal axis strain calculation of the mean coefficients of thermal expansion for Form I during cooling in the range 295 - 130 K.

Table S6. Principal axis strain calculation of the mean coefficients of thermal expansion for Form I during heating in the range 130 - 295 K.

Axes	α (MK ⁻¹)	ασ (ΜΚ-1)	a	b	с
<i>X</i> ₁	6.1617	8.4493	0.2958	-0.0000	0.9553
<i>X</i> ₂	23.5345	5.0754	-0.0000	1.0000	-0.0000
<i>X</i> ₃	14.4733	1.9151	-0.9541	-0.0000	0.2994
V	68.8044	11.3551			

7.2. Forms II and III

In all calculations of the thermal expansivity indicatrix, the phase transitions at 226-225 K and 248-249 K were not taken into account.



Figure S9. The thermal expansivity indicatrix with positive thermal expansion shown in red and very small negative thermal expansion in blue for cooling mode; (a) for Form II in the temperature range of 400-226 K, (b) for Form III in the temperature range of 225-100 K.



Figure S10. The thermal expansivity indicatrix with positive thermal expansion shown in red and very small negative thermal expansion in blue for heating mode. (a) for Form **III** in the temperature range of 100-248 K, (b) for Form **II** in the temperature range of 249-400 K.

Table S7. Principal axis strain calculation of the mean coefficients of thermal expansion during cooling for Form II in the range 400 - 226 K.

Axes	α (MK ⁻¹)	ασ (MK ⁻¹)	a	b	с
X_1	-17.3221	0.9254	0.7673	-0.0000	-0.6413
X_2	28.4209	0.6532	0.4519	-0.0000	0.8921
<i>X</i> ₃	145.4193	3.9593	0.0000	-1.0000	0.0000
V	160.8468	4.1014			



Figure S11. Variation of principal tensor lengths from PASCal with temperature for Form **II** in the cooling range 400 K to 226 K.

Table S8. Principal axis strain calculation of the mean coefficients of thermal expansion for Form III during cooling in the range 225 - 100 K.

Axes	α (MK ⁻¹)	ασ (MK ⁻¹)	a	b	с
X_1	-5. 3307	2.0086	0.6412	0.0000	-0.7674
X_2	59.1395	0.8379	0.5366	0.0000	0.8438
<i>X</i> ₃	98.6145	1.9406	0.0000	-1.0000	0.0000
V	150.0134	1.3546			



Figure S12. Variation of principal tensor lengths from PASCal with temperature for Form **III** in the cooling range 225 to 100 K.

Table S9. Principal axis strain calculation of the mean coefficients of thermal expansion for Form III during heating in the range 100 - 248 K.

Axes	α (MK ⁻¹)	ασ (MK ⁻¹)	a	b	с
X_1	-6.1943	1.3851	0.6503	-0.0000	-0.7597
X_2	58.6512	0.8578	0.5311	-0.0000	0.8473
<i>X</i> ₃	99.1616	2.8425	0.0000	-1.0000	0.0000
V	152.7101	2.5290			



Figure S13. Variation of principal tensor lengths from PASCal with temperature for Form **III** in the heating range 100 to 248 K.

Table S10. Principal axis strain calculation of the mean coefficients of thermal expansion for Form II during heating in the range 249 - 400 K.

Axes	α (MK ⁻¹)	ασ (MK-1)	a	b	c
X ₁	-19.8902	1.1586	-0.7309	0.0000	0.6824
X ₂	28.2130	1.9935	-0.4687	0.0000	-0.8834
X ₃	154.7215	4.6907	0.0000	-1.0000	0.0000
V	162.1752	3.6181			



Figure S14. Variation of principal tensor lengths from PASCal with temperature for Form **II** in the cooling range 249 to 400 K.

9. Hirshfeld surface analysis

In determining the nature of interplay of the three polymorphs of **TI** in the solid state, analysis of close intermolecular interactions has been undertaken using Hirshfeld surface analysis generated by Crystal Explorer.[10] In this study we used the d_e surface, which is the distance from the surface to the nearest atom *exterior* to the surface.



Figure S15. Mapping out the H····H contacts on the Hirshfield surface, and corresponding fingerprint plots for **TI**: a) Form **I** at RT, b) Form **II** at RT and c) Form **III** at 100K.



Figure S16. Mapping out the $H \cdots C$ contacts on the Hirshfield surface and corresponding fingerprint plots for **TI**: a) Form **I** at RT, b) Form **II** at RT and c) Form **III** at 100K.

10. Computational details

Hydrogen atom positions were optimised using the DMol³ module¹¹ within the Biovia Materials Studio software suite,¹² utilising the GGA PBE functional¹³ with the Tkatchenko-Scheffler method¹⁴ for the DFT-D dispersion correction. An all-electron core treatment with the TNP basis set (Triple Numerical plus polarization) was chosen to describe the electronic structure. Molecular dynamics calculations were undertaken using the COMPASS2¹⁵ force field in the Forcite module of the Biovia Materials Studio software suite, ¹² with the atomic charges assigned from the Hirshfeld population analysis calculated during the DMol³

optimisation. The crystal structure data for forms I (at 130 K and 295 K), II (at 295 K and 400 K) and III (at 100 K) were taken as the starting points. A 50.0 ps equilibration run of the unit cell with *P1* symmetry using NVE dynamics was followed by a 500.0 ps production run using the NPT ensemble on a $2 \times 2 \times 2$ supercell. Temperatures were maintained using the Berendsen thermostat. The distance distribution and evolution of all close contacts within 0.95 of the sum of the van der Waals' radii (0.95 sumvdW) were analysed from the equilibrium trajectory documents.

The molecular dynamics runs for Form **III** at varying temperatures (Figure S17) show a change in the thermal expansion of the cell volume between 250 and 300 K. The effect is not as dramatic as found experimentally; the large standard deviation at 300 K suggests that this is most likely due to the molecular dynamics calculation osscilating between Forms **II** and **III**.



Figure S17. Average values of Form **III** cell volume calculated from the last 300 ps of molecular dynamics calculations plotted against temperature.



Figure S18. Distribution of close contacts ≤ 0.95 sumvdW determined from molecular dynamics calculations for Form I at 130 K and Form III at 100 K and 150 K.



Figure S19. Distribution of close contacts ≤ 0.95 sumvdW determined from molecular dynamics calculations for Forms I and II at 295 K and Form III at 300 K.



Figure S20. Distribution of close contacts ≤ 0.95 sumvdW determined from molecular dynamics calculations for Forms I, II and III at 400 K.



Figure S21. Distribution of close contacts ≤ 0.95 sumvdW determined from molecular dynamics calculations for Form III at varying temperatures.

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