

# SUPPLEMENTARY MATERIALS FOR THE ARTICLE:

## OVERT AND HIDDEN POLYMORPHISM IN THE BINARY SYSTEM INVOLVING THE *Z*- AND *E*- ISOMERS OF BROPARESTROL

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Equation S3. Tammann plot of eutectic  $\varepsilon_3$

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Equation S5. Fitted liquidus  $I_E$

Equation S6. Fitted liquidus  $I_Z$

## TABLES

**Table S1. Triple points, temperatures, and pressures in the *E*-broparestrol system**

TRIPLE POINTS	Temperature /K	Pressure /Pa	Constant B <sup>a</sup>
<b>I-Liquid-Vapour</b>	386.7	10.40	31.75
<b>II-Liquid-Vapour</b>	385.4	9.71	33.07
<b>I-II-Vapour</b>	376.6	4.72	-

<sup>a</sup>The constant of the involved polymorph.

The data in **Table S1** have been obtained in the following way. The vapour pressures of *E*-broparestrol forms I and II can be calculated using the Clausius-Clapeyron equation:

$$\ln P = -\frac{\Delta H}{RT} + B$$

in which  $P$  is the vapour pressure of a condensed phase (liquid or forms I or II),  $\Delta H$  the enthalpy of vaporization for the liquid or the enthalpy of sublimation for a solid in J mol<sup>-1</sup>,  $R = 8.314472$  J mol<sup>-1</sup> K<sup>-1</sup> is the gas constant,  $T$  is the absolute temperature, and  $B$  is a constant.

The PhysChem Module of the ACD/Labs Percepta Platform predicts a boiling point of 428.4 °C (701.55 K) and an enthalpy of vaporization of 65.7 kJ mol<sup>-1</sup>.<sup>⊗</sup> Using these values and the fact that the vapour pressure of the liquid at the boiling point is 1×10<sup>5</sup> Pa, the temperature dependence of the vapour pressure is given by the following Clausius-Clapeyron equation:

$$\ln(P/\text{Pa}) = -(7901.88/(T/\text{K})) + 22.78.$$

Since the vapour pressure of the liquid and that of the solids are equal at their respective melting triple points, the vapour pressure dependence on the temperature of each polymorph can be calculated. Using Hess' law, the sublimation enthalpy  $\Delta_{\text{sub}}H_i$  ( $i = \text{I or II}$ ) is obtained by the sum of the melting enthalpy  $\Delta_{\text{fus}}H_i$  and the vaporization enthalpy  $\Delta_{\text{vap}}H$ . Thus, the sublimation enthalpies are  $\Delta_{\text{sub}}H_{\text{I}} = 94546.81$  J mol<sup>-1</sup> and  $\Delta_{\text{sub}}H_{\text{II}} = 98732$  J mol<sup>-1</sup>.

The Clausius-Clapeyron equation above allows to calculate the vapour pressures at the temperatures of fusion approximating the triple points *i*-liquid-vapour and from these pressures the constants  $B_{\text{sub},i}$  can be obtained, hence leading to Clausius-Clapeyron equations for the two solid forms I<sub>E</sub> and II<sub>E</sub>. At triple point I-II-vapor, the vapour pressures of forms I and II are equal. Setting the equations equal of the I-vapour and II-vapour two-phase equilibria, the temperature and the pressure of the I-II vapour equilibrium are found to be 376.6 K and 4.7 Pa, respectively. These results have been compiled in **Table S1**.

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<sup>⊗</sup> ACD/Labs Percepta Platform-PhysChem Module.

<https://www.acdlabs.com/products/percepta-platform/>

**Table S2. Crystal data and structure refinement of *E*-broparestrol form I<sub>E</sub>**

**Crystal data**

C<sub>22</sub>H<sub>19</sub>Br

*M<sub>r</sub>* = 363.29

Monoclinic, *P*2<sub>1</sub>/*c*

*a* = 5.6079(4) Å

*b* = 16.1206(10) Å

*c* = 20.250(1) Å

*β* = 100.569(4)°

*V* = 1799.6(2) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.26 g cm<sup>-3</sup>

Cu *Kα*<sub>1</sub> radiation

*μ* = 0.095 mm<sup>-1</sup>

*T* = 293 K

Specimen shape: cylinder 10×0.5 mm

**Data collection**

Diffractometer INEL CPS 120

Specimen mounting: Lindemann glass capillary 0.5 mm

Specimen mounted in transmission mode

Scan method: curved detector

Absorption correction: none

2θ<sub>min</sub> = 4.0°, 2θ<sub>max</sub> = 75.0°

Increment in 2θ = 0.029°

**Refinement**

Refinement on *I*<sub>net</sub>

*R<sub>p</sub>* = 6.300

*R<sub>wp</sub>* = 8.786

*R<sub>exp</sub>* = 2.033

χ<sup>2</sup> = 4.322

Profile function: modified Thompson-Cox-Hastings pseudo-Voigt

952 reflections

177 parameters

119 restraints

H-atom parameters restrained

Weighting scheme based on measured s.u.'s

*w* = 1/σ(*Y*<sub>obs</sub>)<sup>2</sup>

(Δ/σ)<sub>max</sub> = 0.001

**Table S3. Atom coordinates and equivalent displacement parameters  $B_{\text{iso}}$  in the *E*-broparestrol high-temperature form  $I_E$  at 293 K<sup>a</sup>**

Atom labelling and identification		$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{\text{iso}}(\sigma)/\text{\AA}^2$
C1	C	-0.76721(75)	0.37712(23)	0.32992(19)	11.00(22)
C2	C	-0.55050(89)	0.33322(32)	0.37131(18)	11.00(22)
C3	C	-0.80248(61)	0.46598(25)	0.34852(16)	11.00(22)
C4	C	-0.79320(65)	0.37081(19)	0.25392(18)	11.00(22)
Br5	Br	-0.53532(80)	0.35105(27)	0.46697(19)	11.00(22)
C6	C	-0.53934(63)	0.24137(24)	0.35771(16)	11.00(22)
C7	C	-0.97880(65)	0.48733(24)	0.38716(14)	11.00(22)
C8	C	-0.66458(66)	0.52948(24)	0.32725(17)	11.00(22)
C9	C	-0.61230(66)	0.32991(19)	0.22638(19)	11.00(22)
C10	C	-0.99072(67)	0.40370(19)	0.20806(19)	11.00(22)
C11	C	-0.32939(65)	0.19419(23)	0.38267(15)	11.00(22)
C12	C	-0.74129(66)	0.20076(24)	0.31923(14)	11.00(22)
C13	C	-1.01525(67)	0.56946(24)	0.40398(17)	11.00(22)
H14	H	-1.0900(33)	0.4390(10)	0.40490(87)	13.20(26)
C15	C	-0.69971(65)	0.61059(24)	0.34373(16)	11.00(22)
H16	H	-0.5257(30)	0.51629(98)	0.29747(91)	13.20(26)
C17	C	-0.62797(66)	0.32230(19)	0.15746(19)	11.00(22)
H18	H	-0.4558(29)	0.30378(99)	0.25973(81)	13.20(26)
C19	C	-1.00394(66)	0.39566(16)	0.13907(19)	11.00(22)
H20	H	-1.1379(31)	0.43609(96)	0.22576(83)	13.20(26)
C21	C	-0.32103(67)	0.11081(23)	0.37003(14)	11.00(22)
H22	H	-0.1674(30)	0.2227(10)	0.41246(96)	13.20(26)
C23	C	-0.73292(66)	0.11649(24)	0.30642(15)	11.00(22)
H24	H	-0.9090(32)	0.2345(10)	0.29840(95)	13.20(26)
C25	C	-0.87571(61)	0.63114(24)	0.38232(15)	11.00(22)
H26	H	-1.1529(32)	0.5854(10)	0.43371(89)	13.20(26)
H27	H	-0.5870(35)	0.6583(11)	0.32616(90)	13.20(26)
C28	C	-0.82167(62)	0.35466(18)	0.11300(18)	11.00(22)
H29	H	-0.4889(39)	0.29090(97)	0.13614(94)	13.20(26)
H30	H	-1.1583(33)	0.4214(10)	0.10377(86)	13.20(26)
C31	C	-0.51904(62)	0.07225(24)	0.33255(14)	11.00(22)
H32	H	-0.1600(30)	0.0739(10)	0.38890(84)	13.20(26)
H33	H	-0.8927(33)	0.0855(11)	0.27617(82)	13.20(26)
H34	H	-0.9049(34)	0.69572(98)	0.39531(96)	13.20(26)
C35	C	-0.82953(64)	0.34443(21)	0.03887(18)	11.00(22)
H36	H	-0.5037(34)	0.00619(98)	0.3243(10)	13.20(26)
C37	C	-0.70733(67)	0.41756(24)	0.01226(18)	11.00(22)
H38	H	-0.7389(32)	0.28674(98)	0.02860(80)	13.20(26)
H39	H	-1.0177(32)	0.3396(10)	0.01231(74)	13.20(26)
H40	H	-0.7160(32)	0.4133(10)	-0.04259(89)	13.20(26)
H41	H	-0.5158(37)	0.42045(95)	0.03630(92)	13.20(26)
H42	H	-0.7932(26)	0.4759(14)	0.0231(11)	13.20(26)

<sup>a</sup>esd's in parentheses

**Table S4. Bond lengths in *E*-broparestrol form I<sub>E</sub><sup>a</sup>**

Atom1	Atom2	Length( $\sigma$ )/Å	Atom1	Atom2	Length( $\sigma$ )/Å
C1	C2	1.519(6)	C12	H24	1.10(2)
C1	C3	1.503(5)	C13	C25	1.385(5)
C1	C4	1.522(5)	C13	H26	1.09(2)
C2	Br5	1.945(5)	C15	C25	1.406(5)
C2	C6	1.509(6)	C15	H27	1.10(2)
C3	C7	1.411(5)	C17	C28	1.380(5)
C3	C8	1.398(5)	C17	H29	1.08(2)
C4	C9	1.408(5)	C19	C28	1.399(5)
C4	C10	1.412(5)	C19	H30	1.10(2)
C6	C11	1.415(5)	C21	C31	1.373(5)
C6	C12	1.412(5)	C21	H32	1.09(2)
C7	C13	1.391(5)	C23	C31	1.412(5)
C7	H14	1.10(2)	C23	H33	1.11(2)
C8	C15	1.373(5)	C25	H34	1.09(2)
C8	H16	1.09(2)	C28	C35	1.503(5)
C9	C17	1.388(5)	C31	H36	1.08(2)
C9	H18	1.09(2)	C35	C37	1.512(5)
C10	C19	1.391(5)	C35	H38	1.10(2)
C10	H20	1.09(2)	C35	H39	1.10(2)
C11	C21	1.371(5)	C37	H40	1.10(2)
C11	H22	1.10(2)	C37	H41	1.10(2)
C12	C23	1.385(5)	C37	H42	1.10(2)

<sup>a</sup>esd's in parentheses**Table S5. Bond angles A-O-B in *E*-broparestrol form I<sub>E</sub><sup>a,b</sup>**

Atom A	Atom O	Atom B	Angle( $\sigma$ )/°	Atom A	Atom O	Atom B	Angle( $\sigma$ )/°
C2	C1	C3	115.7(3)	C3	C8	C15	120.7(3)
C2	C1	C4	116.4(3)	C4	C9	C17	121.5(3)
C3	C1	C4	108.9(3)	C4	C10	C19	121.1(3)
C1	C2	Br5	111.4(3)	C6	C11	C21	121.0(3)
C1	C2	C6	114.3(4)	C6	C12	C23	120.4(3)
Br5	C2	C6	109.3(3)	C7	C13	C25	119.2(3)
C1	C3	C7	120.6(3)	C8	C15	C25	120.4(3)
C1	C3	C8	121.0(3)	C9	C17	C28	121.3(3)
C7	C3	C8	118.4(3)	C10	C19	C28	121.0(3)
C1	C4	C9	119.3(3)	C11	C21	C31	119.7(3)
C1	C4	C10	123.9(3)	C12	C23	C31	118.7(3)
C9	C4	C10	116.8(3)	C13	C25	C15	120.1(3)
C2	C6	C11	121.5(3)	C17	C28	C19	118.3(3)
C2	C6	C12	120.0(3)	C17	C28	C35	119.1(3)
C11	C6	C12	118.6(3)	C19	C28	C35	122.6(3)
C3	C7	C13	121.1(3)	C21	C31	C23	121.6(3)

<sup>a</sup>esd's in parentheses<sup>b</sup>Bond angles involving H-atoms not listed

**Table S6. Torsion angles in *E*-broparestrol form I<sub>E</sub><sup>a,b</sup>**

Atom 1	Atom 2	Atom 3	Atom 4	Torsion angle( $\sigma$ )/ $^{\circ}$	Atom 1	Atom 2	Atom 3	Atom 4	Torsion angle( $\sigma$ )/ $^{\circ}$
C3	C1	C2	Br5	47.6(4)	C1	C4	C10	C19	-179.9(3)
C3	C1	C2	C6	172.2(3)	C9	C4	C10	C19	0.0(5)
C4	C1	C2	Br5	177.5(3)	C2	C6	C11	C21	-180.0(4)
C4	C1	C2	C6	-57.9(5)	C12	C6	C11	C21	-0.1(5)
C2	C1	C3	C7	-101.7(4)	C2	C6	C12	C23	180.0(3)
C2	C1	C3	C8	79.2(5)	C11	C6	C12	C23	0.1(5)
C4	C1	C3	C7	124.8(4)	C3	C7	C13	C25	0.0(5)
C4	C1	C3	C8	-54.2(4)	C3	C8	C15	C25	-0.1(5)
C2	C1	C4	C9	-3.7(5)	C4	C9	C17	C28	0.1(5)
C2	C1	C4	C10	176.2(4)	C4	C10	C19	C28	0.0(5)
C3	C1	C4	C9	129.4(3)	C6	C11	C21	C31	0.0(5)
C3	C1	C4	C10	-50.7(5)	C6	C12	C23	C31	-0.0(5)
C1	C2	C6	C11	168.6(3)	C7	C13	C25	C15	0.1(5)
C1	C2	C6	C12	-11.4(5)	C8	C15	C25	C13	-0.0(5)
Br5	C2	C6	C11	-65.8(4)	C9	C17	C28	C19	-0.1(5)
Br5	C2	C6	C12	114.3(4)	C9	C17	C28	C35	-179.9(3)
C1	C3	C7	C13	-179.2(3)	C10	C19	C28	C17	0.0(5)
C8	C3	C7	C13	-0.1(5)	C10	C19	C28	C35	179.8(3)
C1	C3	C8	C15	179.2(3)	C11	C21	C31	C23	0.0(5)
C7	C3	C8	C15	0.1(5)	C12	C23	C31	C21	-0.0(5)
C1	C4	C9	C17	179.8(3)	C17	C28	C35	C37	-90.6(4)
C10	C4	C9	C17	-0.1(5)	C19	C28	C35	C37	89.6(4)

<sup>a</sup>esd's in parentheses<sup>b</sup>Torsion angles involving H-atom not listed**Table S7. Lattice parameters, volume of the asymmetric unit ( $Z = 4$ ) and specific volume of *E*-broparestrol form I<sub>E</sub> as a function of temperature<sup>a</sup>**

$T/K$	$a(\sigma)/\text{\AA}$	$b(\sigma)/\text{\AA}$	$c(\sigma)/\text{\AA}$	$\beta(\sigma)/^{\circ}$	$V/Z(\sigma)/(\text{\AA}^3)$	$v(\sigma)/\text{cm}^3\text{g}^{-1}$
150	5.546(2)	16.032(3)	20.057(3)	100.17(3)	438.8(2)	0.7272(3)
180	5.560(2)	16.041(3)	20.097(3)	100.20(2)	441.1(2)	0.7308(3)
230	5.575(2)	16.068(3)	20.174(3)	100.29(3)	444.6(2)	0.7367(3)
250	5.584(2)	16.080(2)	20.204(3)	100.33(2)	446.2(2)	0.7393(3)
270	5.600(2)	16.093(2)	20.241(3)	100.45(3)	448.5(2)	0.7431(3)
290	5.609(2)	16.110(2)	20.278(3)	100.48(3)	450.5(2)	0.7464(3)
310	5.620(2)	16.122(2)	20.311(3)	100.57(2)	452.3(2)	0.7494(3)
330	5.627(2)	16.128(2)	20.349(3)	100.75(2)	453.6(2)	0.7516(3)
350	5.643(2)	16.144(2)	20.387(4)	100.89(3)	455.9(2)	0.7555(3)
360	5.659(2)	16.145(2)	20.401(4)	101.02(4)	457.4(2)	0.7578(4)
370	5.665(2)	16.150(2)	20.418(4)	101.15(3)	458.2(2)	0.7592(3)
375	5.675(2)	16.152(2)	20.420(4)	101.19(3)	459.0(2)	0.7605(3)
380	5.682(2)	16.151(2)	20.422(4)	101.18(3)	459.6(2)	0.7616(3)

<sup>a</sup>esd's in parentheses

**Table S8. Lattice parameters, volume of the asymmetric unit ( $Z = 4$ ) and specific volume of *E*-broparestrol form II<sub>F</sub> as a function of temperature<sup>a</sup>**

$T/K$	$a(\sigma)/\text{Å}$	$b(\sigma)/\text{Å}$	$c(\sigma)/\text{Å}$	$\beta(\sigma)/^\circ$	$V/Z(\sigma)/(\text{Å}^3)$	$v(\sigma)/\text{cm}^3\text{g}^{-1}$
130	8.477(1)	35.490(6)	5.681(1)	86.14(1)	426.3(1)	0.7063(2)
180	8.503(1)	35.583(5)	5.702(1)	86.12(1)	430.3(1)	0.7130(2)
230	8.527(1)	35.680(5)	5.722(1)	86.10(1)	434.2(1)	0.7195(2)
250	8.537(1)	35.71(5)	5.731(1)	86.09(1)	435.9(1)	0.72223(15)
270	8.546(1)	35.761(5)	5.739(1)	86.08(1)	437.5(1)	0.72490(15)
290	8.557(1)	35.808(5)	5.748(1)	86.08(1)	439.5(1)	0.72790(15)
296.7	8.562(1)	35.840(5)	5.752(1)	86.07(1)	440.3(1)	0.72952(15)
310	8.570(1)	35.872(5)	5.759(1)	86.08(1)	441.5(1)	0.73162(15)
330	8.580(5)	35.921(5)	5.769(1)	86.09(1)	443.4(1)	0.73471(17)
350	8.586(1)	35.977(5)	5.783(1)	86.08(1)	445.6(1)	0.73831(17)
360	8.591(1)	36.009(5)	5.789(1)	86.08(1)	446.7(1)	0.74016(17)
370	8.597(1)	36.052(5)	5.799(1)	86.10(1)	448.3(1)	0.74283(17)
375	8.595(1)	36.064(5)	5.801(1)	86.09(1)	448.5(1)	0.7432(2)
380	8.600(1)	36.076(6)	5.805(1)	86.08(1)	449.2(1)	0.7443(2)

<sup>a</sup>esd's in parentheses

**Table S9. Lattice parameters, volume of the asymmetric unit ( $Z = 2$ ) and specific volume of *Z*-broparestrol as a function of temperature<sup>a</sup>**

$T/K$	$a(\sigma)/\text{Å}$	$b(\sigma)/\text{Å}$	$c(\sigma)/\text{Å}$	$\alpha(\sigma)/^\circ$	$\beta(\sigma)/^\circ$	$\gamma(\sigma)/^\circ$	$V/Z(\sigma)/(\text{Å}^3)$	$v(\sigma)/\text{cm}^3\text{g}^{-1}$
130	8.020(1)	9.390(2)	11.360(2)	91.711(15)	88.52(1)	90.588(15)	427.40(10)	0.7082(2)
180	8.040(2)	9.411(2)	11.416(2)	91.676(15)	88.80(1)	90.642(15)	431.57(15)	0.7151(2)
230	8.058(2)	9.428(2)	11.475(2)	91.613(15)	89.10(1)	90.686(20)	435.63(15)	0.7218(2)
250	8.070(2)	9.440(2)	11.505(2)	91.574(15)	89.22(1)	90.707(15)	437.97(15)	0.7257(2)
270	8.079(2)	9.451(2)	11.535(2)	91.547(15)	89.37(1)	90.743(15)	440.18(15)	0.7294(2)
292.5	8.090(2)	9.459(2)	11.564(2)	91.476(15)	89.53(1)	90.794(15)	442.25(15)	0.7328(2)
310	8.098(2)	9.469(2)	11.588(2)	91.465(15)	89.63(1)	90.808(15)	444.12(15)	0.7359(2)
330	8.110(1)	9.480(2)	11.621(2)	91.412(15)	89.75(1)	90.855(15)	446.61(15)	0.7400(2)
350	8.122(1)	9.491(2)	11.652(2)	91.354(15)	89.89(2)	90.891(15)	448.95(15)	0.7439(2)
360	8.130(1)	9.502(2)	11.675(2)	91.291(15)	89.95(2)	90.950(15)	450.81(15)	0.7470(2)
370	8.139(2)	9.513(2)	11.695(2)	91.251(15)	90.02(2)	90.978(15)	452.56(15)	0.7499(3)
375	8.146(2)	9.51(2)	11.709(2)	91.241(15)	90.09(1)	90.963(15)	453.44(15)	0.7513(2)

<sup>a</sup>esd's in parentheses



**Table S10. DSC data of physical mixtures of the *E* and *Z* isomers of broparestrol as a function of the mole fraction of *Z* ( $x_Z$ ) after annealing at 323 K for a week<sup>a</sup>**

$x(Z)$	$T_{\text{eutexy } \varepsilon_1} / \text{K}$	$T_{\text{liquidus1}} / \text{K}$ Experimental	$T_{\text{liquidus1}} / \text{K}$ Schröder eq.	$\Delta H_{\varepsilon_1} / \text{J g}^{-1}$	Total enthalpy (eutexy + liquidus) / $\text{J g}^{-1}$
1.00	-	-	385.5	0.00	-
0.96	363.0	385.0	384.0	10.69	87.45
0.85	363.0	383.0	379.5	23.06	87.01
0.74	362.0	379.0	374.6	57.47	88.99
0.61	363.0	374.0	367.9	74.46	89.14
0.49	363.0	367.0	360.6	86.42	92.96
0.47	364.0	367.0	359.3		88.98
0.37	363.0	368.0	368.8	88.00	91.00
0.22	363.0	375.0	376.3	60.79	86.74
0.10	363.0	381.0	381.5	26.55	89.93
0.00	-	385.4	385.4	0.00	-
Mean $T$ ( $\sigma$ )	363.0(0.5)				

<sup>a</sup>Onset temperature and enthalpy of the eutectic equilibrium,  $\varepsilon_1$ , the temperature of the DSC peak maximum for the liquidus curves and the total enthalpy of the eutectic and the liquidus.

**Table S11. DSC data of melted *E*- and *Z*-isomer of broparestrol left to recrystallise at room temperature for three years<sup>a</sup>**

$x_Z$	$T_{\text{eutexy } \varepsilon_2} / \text{K}$	$T_{\text{liquidus2}} / \text{K}$ Experimental	$T_{\text{liquidus2}} / \text{K}$ Schröder eq.	$\Delta H_{\varepsilon_2} / \text{J g}^{-1}$	Total enthalpy (eutexy + liquidus) / $\text{J g}^{-1}$
1	-	385.5	385.5	0.00	
0.96	356.5	383.5	384.0	5.224	88.10
0.85	356.0	381.0	379.5	13.98	82.98
0.74	358.0	375.0	374.6	36.78	80.85
0.74	358.0	375.0	374.6	34.60	76.69
0.49	359.0	363.0	360.7	77.47	83.62
0.47	359.0	- <sup>b</sup>	359.3	80.08	82.28
0.444 <sup>c</sup>	358.1	358.1	357.5	82.94	82.94
0.444 <sup>c</sup>			357.5		
0.37	358.0	365.5	367.8	70.98	83.94
0.22	359.0	374.0	376.3	36.89	76.44
0.10	359.5	380.0	382.2	19.13	88.99
0.00	-	386.7	386.7	0.00	-
Mean $T$ ( $\sigma$ )	358.1(1.1)				

<sup>a</sup> Onset temperature and enthalpy of the eutectic equilibrium,  $\varepsilon_2$ , the temperature of the DSC peak maximum for the liquidus curves and the total enthalpy of the eutectic and the liquidus.

<sup>b</sup> The temperature of the liquidus could not be determined because the peak was convoluted with that of the eutectic event.

<sup>c</sup> Mole fraction of the eutectic liquid obtained from the Tammann plot.

**Table S12. DSC data of melted *E*- and *Z*-isomer of broparestrol left to crystallize for several days<sup>a</sup>**

$x_Z$	$T_{\text{eutexy}\epsilon_3} / \text{K}$	$T_{\text{liquidus3}} / \text{K}$ Experimental	$T_{\text{liquidus3}} / \text{K}$ Schröder eq	$\Delta H_{\epsilon_3} / \text{J g}^{-1}$	Total enthalpy (from eutexy to isotropic liquid) $/\text{J g}^{-1}$
1.00		385.5	385.5	0.00	
0.96	338.4	384.9	384.0	3.40	<b>67.83<sup>b</sup></b>
0.92	337.7	383.0	382.4	10.80	<b>64.43<sup>b</sup></b>
0.85	339.6	383.1	379.5	11.85	-
0.795	340.0	<b>348.4</b>	377.1	39.96	<b>61.64</b>
0.74	340.5	<b>347.1</b>	374.6	45.62	<b>59.37<sup>c</sup></b>
0.74	340.5	<b>347.9</b>		46.86	<b>58.78<sup>c</sup></b>
0.74	340.4	<b>346.4</b>	374.6	47.42	<b>60.72<sup>c</sup></b>
0.684	340.0	<b>340.0</b>		58.52	<b>58.52<sup>d</sup></b>
0.65	340.4	346.0	346.2	58.63	59.58
0.61	341.0	348.5	350.0	50.66	60.00
0.49	340.8	360.2	359.7	44.49	66.67
0.47	341.7	360.3	361.1	35.90	69.05
0.47	341.6	361.0	361.1	39.25	64.58
0.37	341.5	366.5	367.8	32.15	69.48
0.37	339.8	366.0		31.50	68.39
0.326	340.2	369.3	370.4	25.53	71.12
0.22	340.6	376.3	376.3	12.07	61.00
0.176	339.6	377.5	378.5	9.215	64.89
0.10	340.6	382.0	382.2	0.143	64.04
0.03		386.0	385.4	-	71.04
0.0		386.7	386.7	0	
Mean $T(\sigma)$	340.2(1.1)				

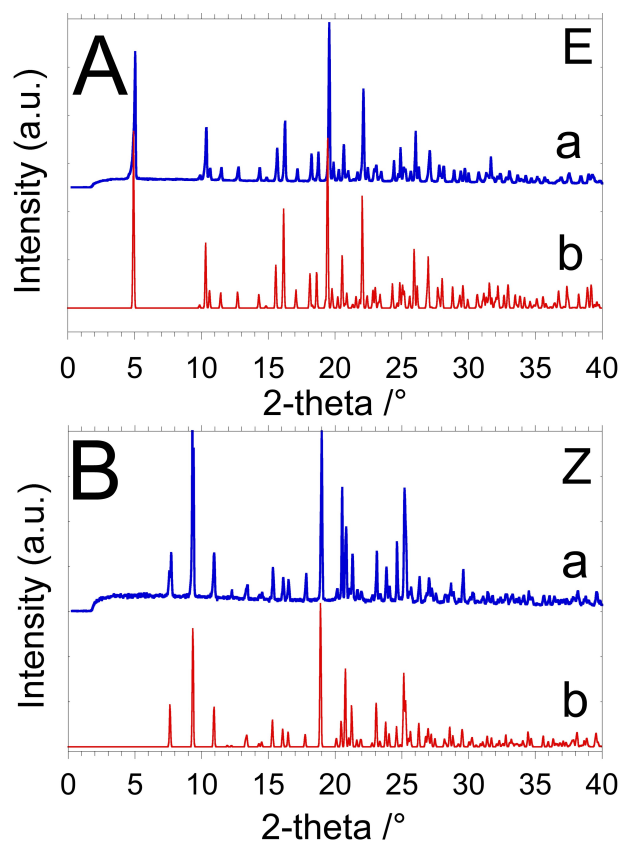
<sup>a</sup> Onset temperature and enthalpy of the eutectic equilibrium,  $\epsilon_3$ , the temperature of the DSC peak maximum for the liquidus curves and the total enthalpy of the eutectic and the liquidus.

<sup>b</sup> The exothermic part of the DSC curve was subtracted from the endothermic part.

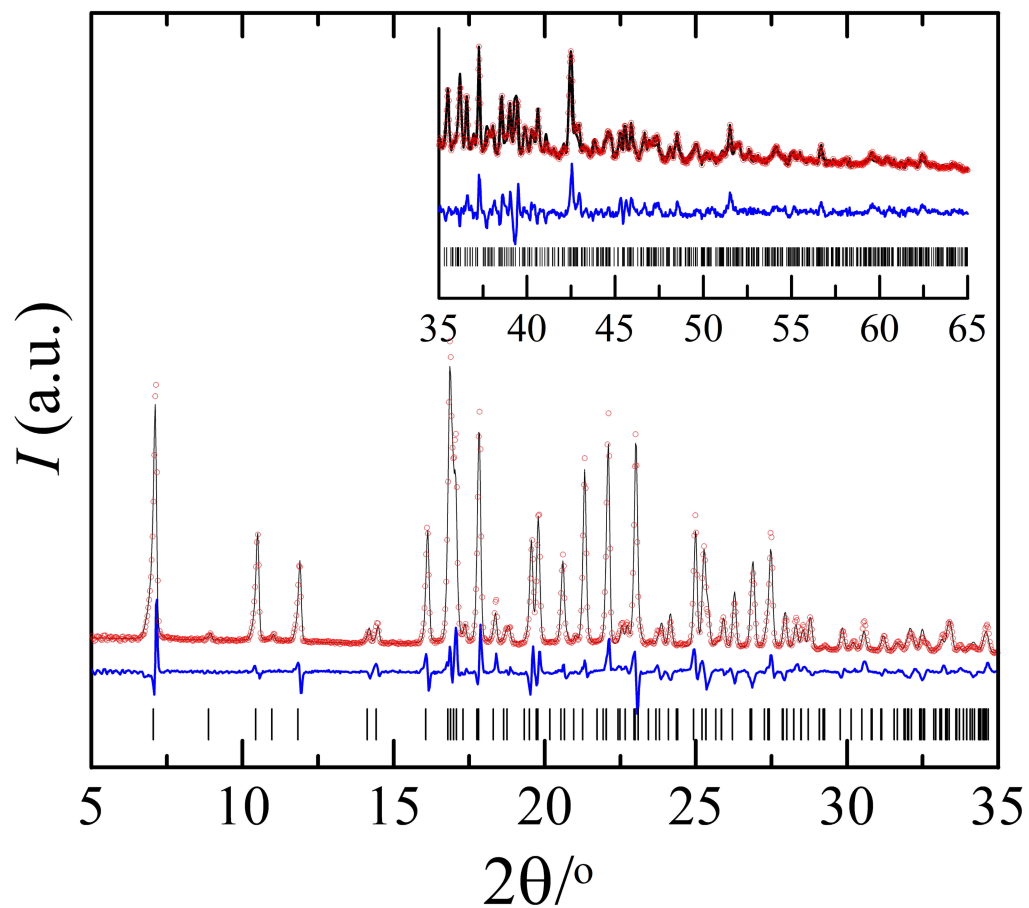
<sup>c</sup> Results of three measurements

<sup>d</sup> Extrapolated using the Tammann plot in Figure S9c

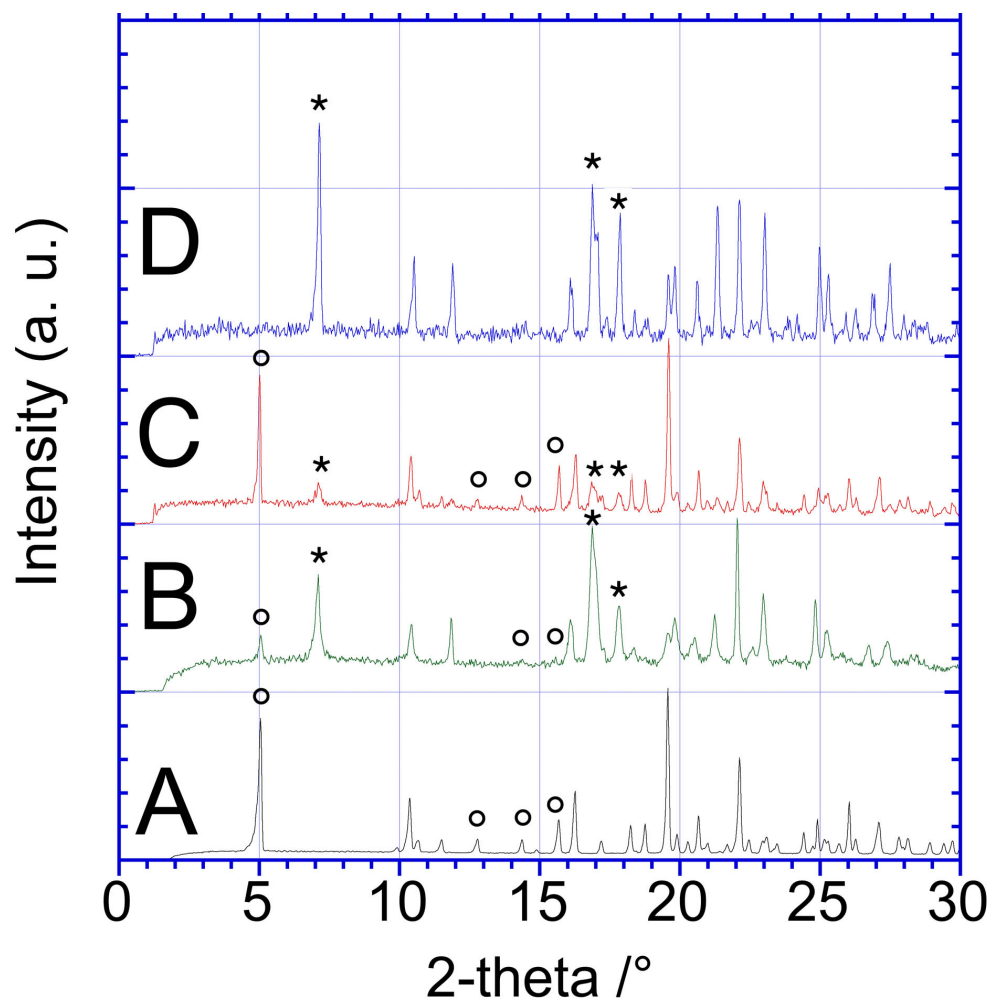
## FIGURES



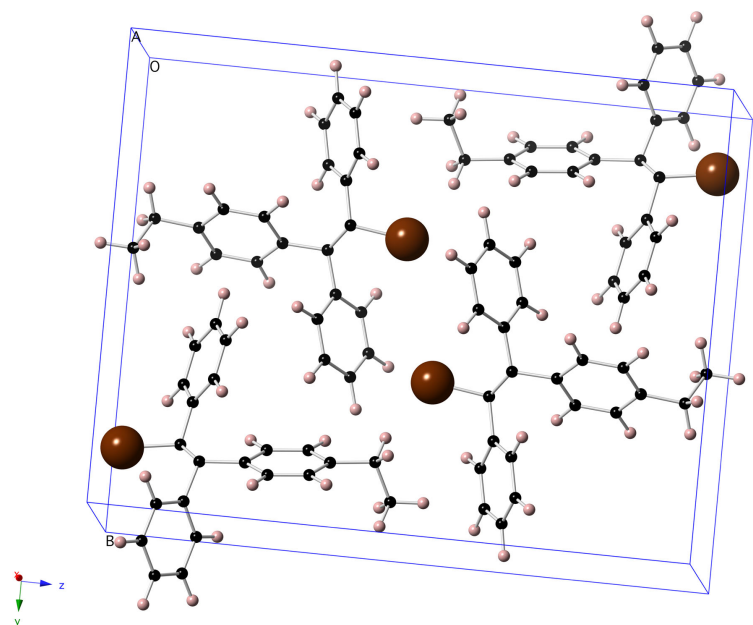
**Figure S1.** (A) Experimental (a) and calculated (b, from the known crystal structure) powder X-ray diffraction patterns of the as-received monoclinic *E*-broparestrol II<sub>E</sub> and (B) from the triclinic *Z*-broparestrol I<sub>Z</sub>.



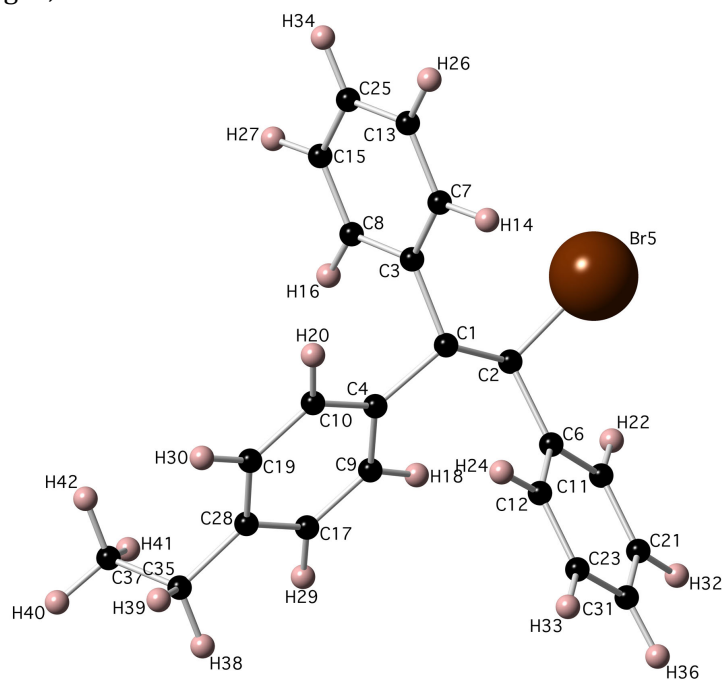
**Figure S2.** Experimental (red) and fitted diffraction pattern (black) of the new polymorph of *E*-broparestrol,  $I_E$ , with residuals (blue) and tick marks (black) for the peak positions



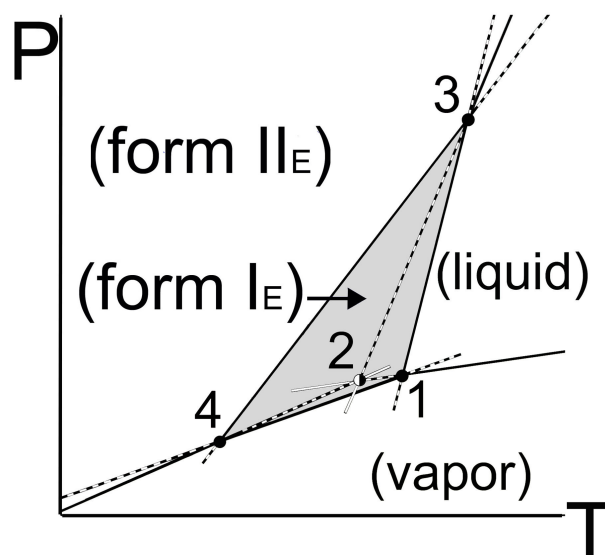
**Figure S3.** Powder X-ray diffraction patterns of *E*-broparestrol. (A) as-received monoclinic sample II<sub>E</sub>, (D) the new polymorph, I<sub>E</sub>, and (B and C) patterns obtained at room temperature soon after recrystallization from the melt, which correspond to mixtures of the known polymorph II<sub>E</sub> (peaks marked by ‘o’) and the new polymorph I<sub>E</sub> (peaks marked by ‘\*’)



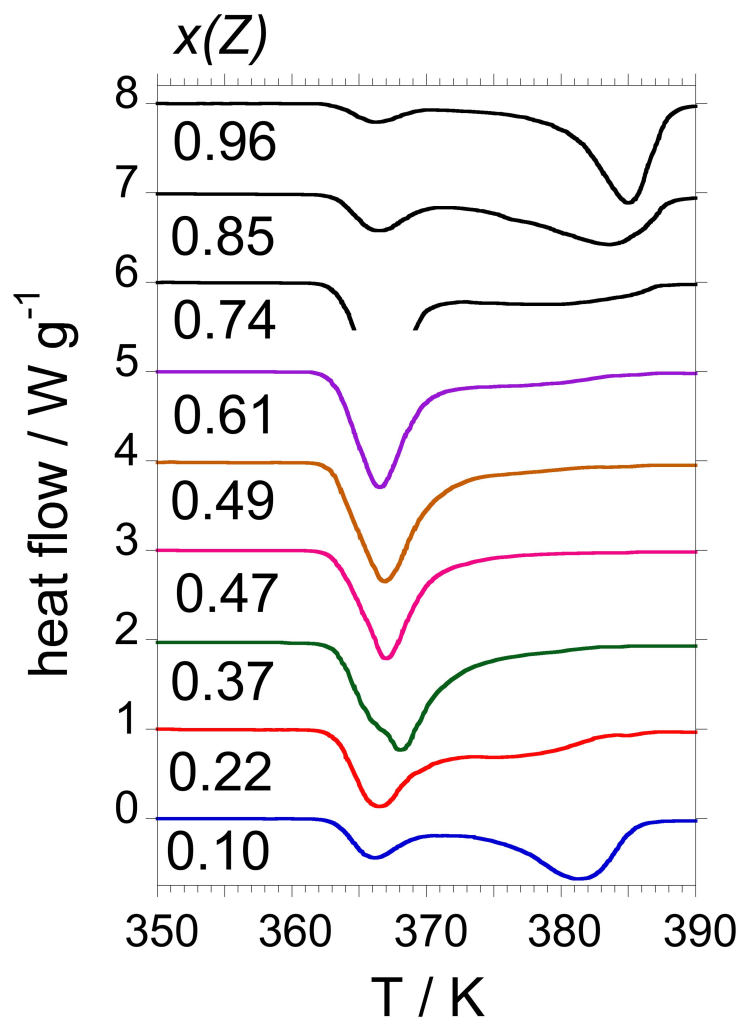
**Figure S4a.** Projection of the unit-cell of form I<sub>E</sub> of *E*-broparestrol on the bc plane with black: carbon, pink: hydrogen, and brown: bromine



**Figure S4b.** Molecular structure and atom numbering of *E*-broparestrol form I<sub>E</sub>; black: carbon, pink: hydrogen, brown: bromine.

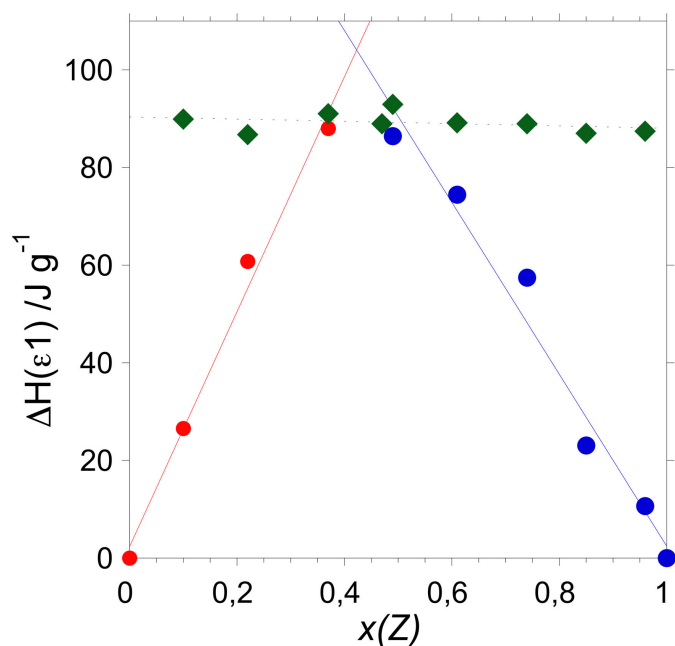


**Figure S5.** Topological  $P$ - $T$  phase diagram presenting the stability regions of form I<sub>E</sub> (grey area) and of form II<sub>E</sub> of *E*-broparestrol with triple points 1: I<sub>E</sub>-liquid-vapour (stable), 2: II<sub>E</sub>-liquid-vapour (metastable), 3: I<sub>E</sub>-II<sub>E</sub>-liquid (stable), and 4: I<sub>E</sub>-II<sub>E</sub>-vapor (stable) and two-phase equilibrium lines 1-4: I<sub>E</sub>-vapor, 2-4: II<sub>E</sub>-vapor, 1-3: I<sub>E</sub>-liquid, 2-3: II<sub>E</sub>-liquid, 3-4: I<sub>E</sub>-II<sub>E</sub>, and 1-2: liquid-vapour with solid lines: stable phase equilibria and dashed lines: metastable. Such a diagram is topologically the same as the  $P$ - $T$  diagram for the dimorphism of elemental sulfur.

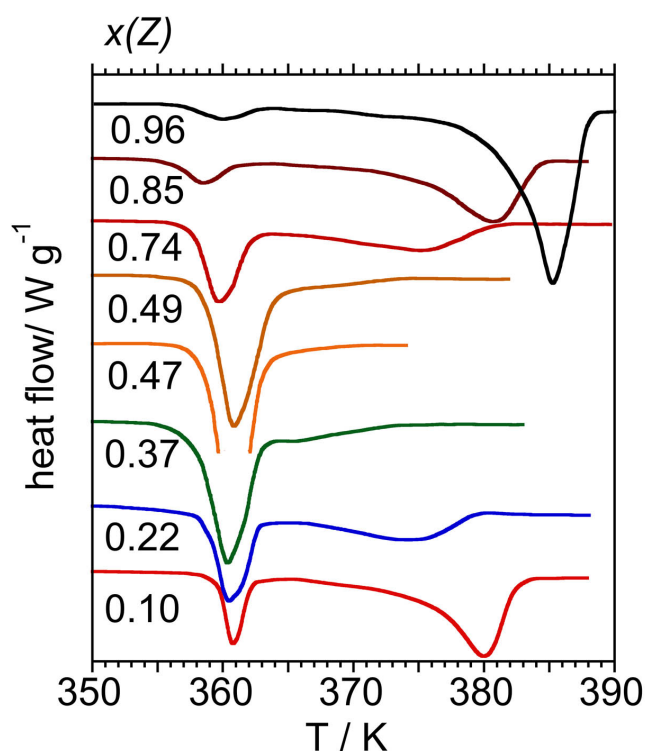


**Figure S6a.** Temperature-composition data for the  $T$ - $x$  phase diagram involving the two isomers of broparestrol. The first series of DSC curves obtained with mixtures of form  $\text{II}_E$  and triclinic  $Z$ -bropestrol after annealing at 323 K for one week.  $x(Z)$  is the mole fraction of  $Z$ -bropestrol. A eutectic equilibrium  $\varepsilon_1$  is observed at 363 K (onset).

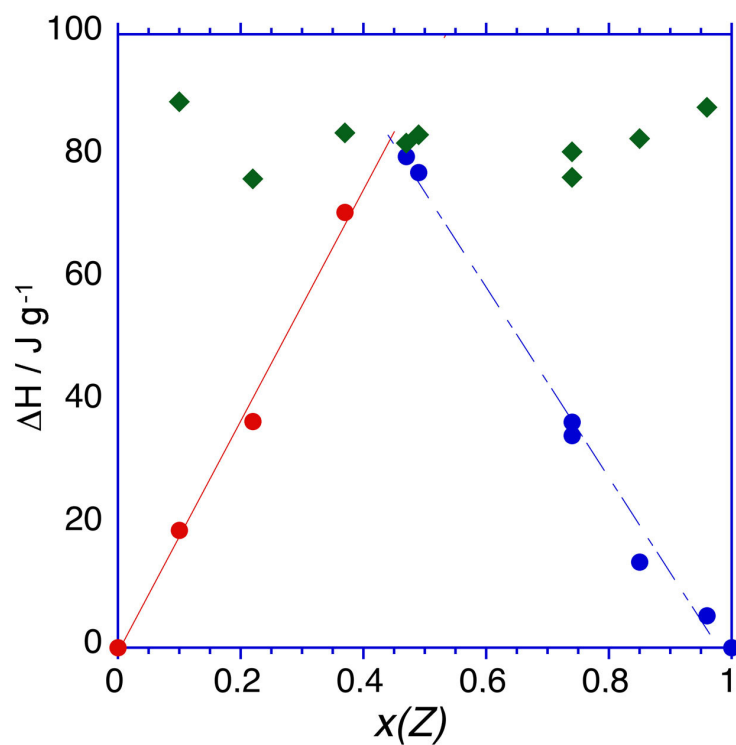




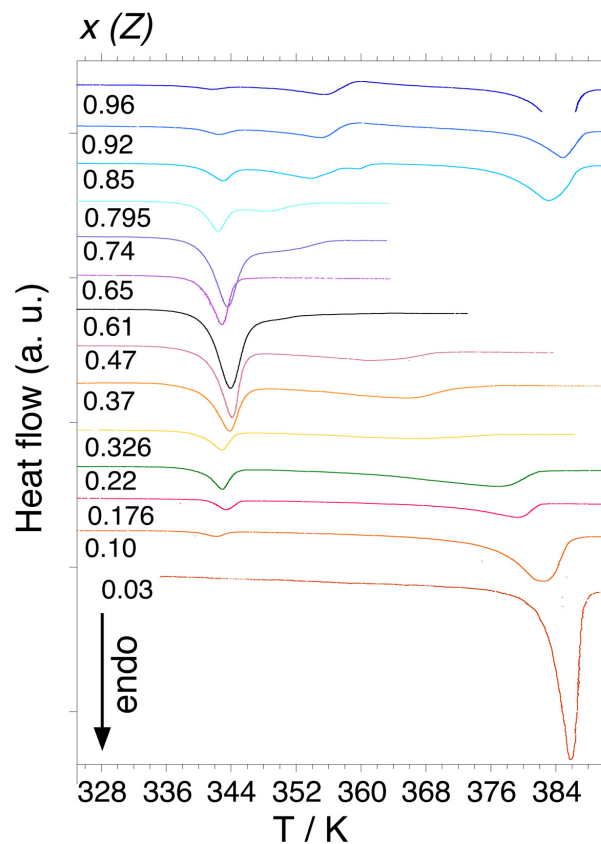
**Figure S6b.** The Tammann plot of the eutectic equilibrium  $\epsilon_1$  (red and blue filled circles) observed at 363 K and the total endothermic effect obtained by summing over the eutexy and liquidus peaks (filled diamonds).



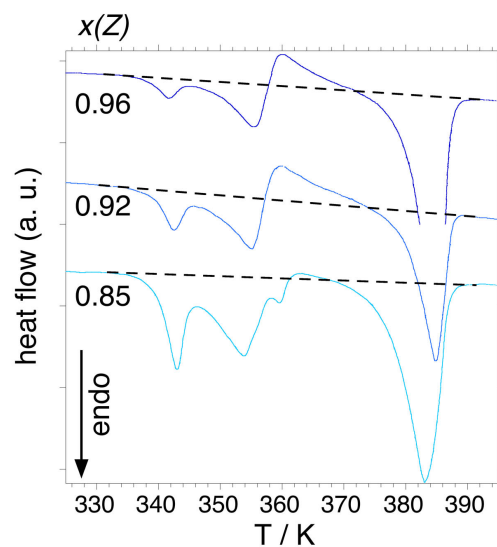
**Figure S7a.** Temperature-composition data for the  $T$ - $x$  phase diagram involving the two isomers of broparestrol. The second series of DSC curves obtained with mixtures of form  $I_E$  and triclinic  $Z$ -broparestrol melted and then recrystallized during annealing for three years at room temperature.  $x(Z)$  is the mole fraction of  $Z$ -broparestrol. A eutectic equilibrium  $\epsilon_2$  is observed at 358.1 K (onset).



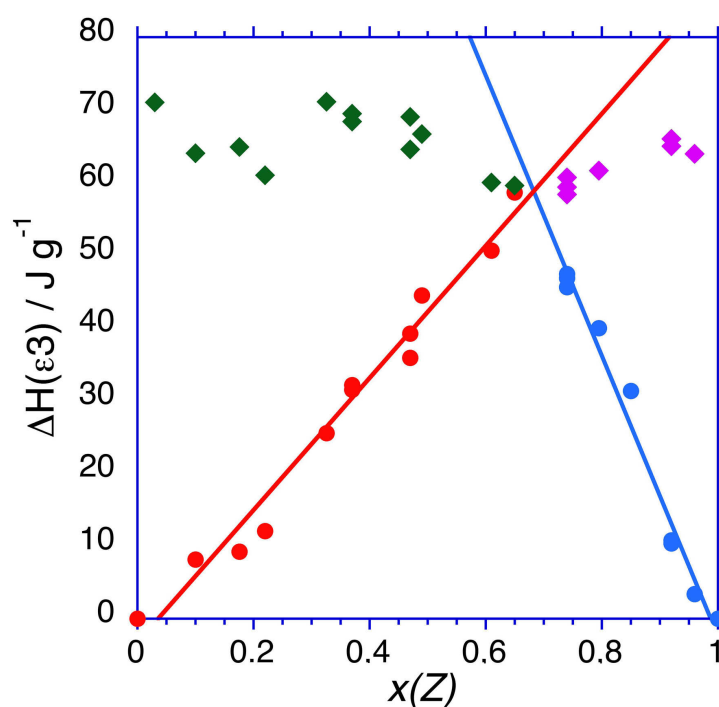
**Figure S7b.** The Tammann plot of the eutectic equilibrium  $\varepsilon_2$  (red and blue filled circles) observed at 358.1 K and the total endothermic effect obtained by summing over the eutaxy and liquidus peaks (filled diamonds).



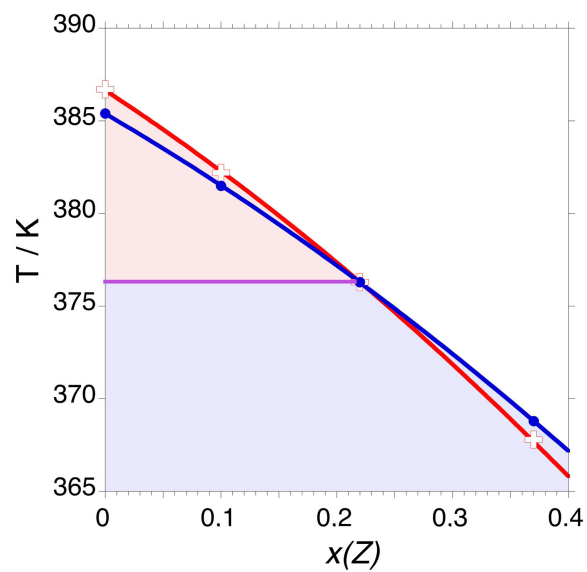
**Figure S8a.** Temperature-composition data for the  $T$ - $x$  phase diagram involving the two isomers of bropestrol. The third series of DSC curves obtained with mixtures of form  $I_E$  and triclinic  $Z$ -bropestrol melted and recrystallized for a few days at room temperature.  $x(Z)$  is the mole fraction of  $Z$ -bropestrol. A eutectic equilibrium  $\varepsilon_3$  is observed at 340 K (onset) for most mixtures except for  $x_Z = 0.03$ .



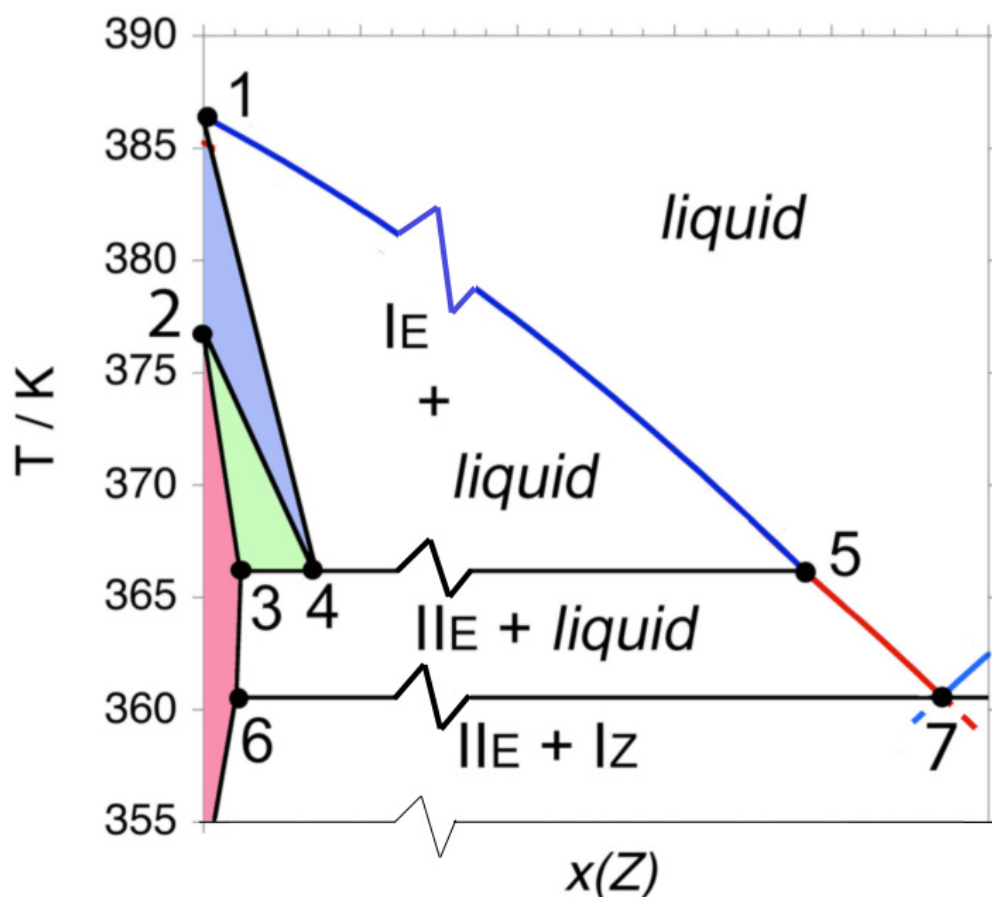
**Figure S8b.** Close-ups from Figure S8a showing the exothermic recrystallization (above the dashed baseline) into the stable Z-isomer polymorph from metastable states in which the metastable polymorph of the Z-isomer plays a role.



**Figure S8c.** The Tammann plot of the eutectic equilibrium  $\varepsilon_3$  (red and blue filled circles) observed at 340 K and the total endothermic effect obtained by summing over the eutaxy and liquidus peaks (green and violet filled diamonds). The two lines cross at 0.684 with an enthalpy of 58.52 J g<sup>-1</sup>. Together with the eutectic point (see values in bold in Table S12), the total enthalpies of the Z-rich side were fitted to a straight line:  $\Delta H = 35.828 + 32.279 x_Z$  ( $r^2 = 0.92$ ). With this equation, a tentative value of 68.1 J g<sup>-1</sup> is found for the melting enthalpy of the metastable form of the Z-isomer.



**Figure S9.** Close-up of the  $E$ -rich side of the ideal  $T$ - $x$  phase diagram demonstrating the intersection of the two ideal liquidus curves in equilibrium with forms  $I_E$  (red) and form  $II_E$  (blue) at about 377 K. The violet horizontal line corresponds to the invariant 3-phase equilibrium involving ideal pure polymorphs  $I_E$ ,  $II_E$  and the liquid phase. This line separates two 2-phase regions:  $I_E$  + liquid (light-red area) and  $II_E$  + liquid (light-blue area).



**Figure S10.** Qualitative drawing of the  $E$ -rich side of the  $T$ - $x$  phase diagram between  $E$ - and  $Z$ -isomers of broparestrol showing the magnified extent of the limited solid solutions of form  $I_E$  (blue area) and form  $II_E$  (red area). The green area corresponds to the  $T$ - $x$  range where the two polymorphs as solid solutions are in equilibrium with each other.

1: melting temperature of pure form  $I_E$ , 2: temperature of transition from pure form  $II_E$  to pure form  $I_E$  on heating, line 3-4-5: metatectic equilibrium between solid solution form  $II_E$  (point 3), solid solution form  $I_E$  (point 4) and the metatectic liquid (point 5), line 6-7: part of the eutectic equilibrium between solid solution form  $II_E$  (point 6), form  $I_Z$  (not shown) and the eutectic liquid (point 7). No  $x_Z$  values have been provided as the graph is qualitative and the exact concentrations of the solid solutions in equilibrium with the liquid are not known.

## EQUATIONS

Tammann plot fits for the eutectic  $\varepsilon_1$ :

$$Z\text{-rich side: } \Delta H_{\varepsilon_1-Z} / Jg^{-1} = 178.39 - 175.97 \times x_Z \quad (r^2 = 0.97) \quad (S1a)$$

$$E\text{-rich side: } \Delta H_{\varepsilon_1-E} / Jg^{-1} = 2.3521 + 240.48 \times x_Z \quad (r^2 = 0.99) \quad (S1b)$$

Tammann plot fits for the eutectic  $\varepsilon_2$ :

$$Z\text{-rich side: } \Delta H_{\varepsilon_2-Z} / Jg^{-1} = 151.84 - 155.19 \times x_Z \quad (r^2 = 0.996) \quad (S2a)$$

$$E\text{-rich side: } \Delta H_{\varepsilon_2-E} / Jg^{-1} = -0.77996 + 188.58 \times x_Z \quad (r^2 = 0.996) \quad (S2b)$$

Tammann plot fits for the eutectic  $\varepsilon_3$ :

$$Z\text{-rich side: } \Delta H_{\varepsilon_3-Z} / Jg^{-1} = 190.26 - 192.64 \times x_Z \quad (r^2 = 0.991) \quad (S3a)$$

$$E\text{-rich side: } \Delta H_{\varepsilon_3-E} / Jg^{-1} = -3.2623 + 90.942 \times x_Z \quad (r^2 = 0.988) \quad (S3b)$$

### Empirical equations for the experimental and ideal liquidus curves of the stable $T$ - $x$ phase diagram involving the two isomers of broparestrol

In **Figure 10**, the stable  $T$ - $x$  phase diagram has been drawn using experimental liquidus curves obtained with three series of experiments:

**Curve 1:** the  $E$ -rich side liquidus from the first measurement series (see **Table S10** for the liquidus in equilibrium with form  $II_E$ ),

**Curve 2:** the  $E$ -rich side liquidus curve from the third measurement series (see **Table S12** for the compositions of the liquidus in equilibrium with form  $I_E$ ), and

**Curve 3:** the  $Z$ -sided liquidus curve from the second measurement series (see **Table S11** for the compositions of the liquidus in equilibrium with form  $I_Z$ ).

These experimental curves were fitted to empirical quadratic functions:

$$\text{Curve 1 - liquidus } II_E: T/K = 385.26 - 38.447 \times x_Z - 29.71 \times x_Z^2 \quad (r^2 = 0.995) \quad (S4),$$

$$\text{Curve 2 - liquidus } I_E: T/K = 386.49 - 37.286 \times x_Z - 40.72 \times x_Z^2 \quad (r^2 = 0.995) \quad (S5),$$

$$\text{Curve 3 - liquidus } I_Z: T/K = 323.46 + 94.313 \times x_Z - 32.511 \times x_Z^2 \quad (r^2 = 0.995) \quad (S6).$$

By setting the equations of curves 1 and 2 equal (**Eqs. S4** and **S5**), the composition of the liquid of the horizontal equilibrium curve  $I_E$ - $II_E$ -liquid is  $x_Z = 0.391$  at a temperature  $T(I_E$ - $II_E$ -liquid) = 365.7 K (see horizontal line 3-4-5 in **Figure S10**).

By setting the equations of curves 1 and 3 equal (**Eqs. S4** and **S6**), the intersection -which corresponds to the stable eutectic liquid- is found at  $x_Z = 0.470$  and  $T\varepsilon = 360.6$  K (see horizontal line 6-7 in **Figure S10**).