Supplementary information for "Crystal structures of alkyl-substituted Tröger's base derivatives illustrate the importance of Z' for packing in the absence of strong crystal synthons".

Christophe M.L. Vande Velde[a,b]*, Benoît Tylleman[b], Matthias Zeller[c] and Sergey Sergeyev[d,b]*

[a]Karel de Grote University College, Department of Applied Engineering, Salesianenlaan 30, 2660 Antwerp, Belgium

[b]Université Libre de Bruxelles (ULB), Laboratoire de Chimie des Polymères, CP 206/01, Boulevard du Triomphe, 1050 Brussels, Belgium

[c]Youngstown State University, Department of Chemistry, One University Plaza, Youngstown, OH 44555-3663, U.S.A.

[d]University of Antwerp, Department of Chemistry, Groenenborgerlaan 171, 2020 Antwerp, Belgium

*corresponding authors, christophe.vandevelde@kdg.be, serguei.sergueev@ua.ac.be

Table S1: Intermolecular contacts shorter than the van der Waals radii in the structure of **α -3a**

A	H	B	Symm. eq. B	H…B (Å)	A-H…B (°)	A…Cg[a] (Å)
Res. 1						
C3	H3	N25	x,y,z	2.694(12)	162.2(9)	
C13	H13A	C1	2-x,-y,1-z	2.771(5)	138.8(5)	
C13	H13A	C2	2-x,-y,1-z	2.855(5)	139.0(5)	
C13	H13A	C12A	2-x,-y,1-z	2.831(5)	147.5(4)	
C13	H13B	H15A	2-x,-y,1-z	2.399(12)	136.8(6)	
C16	H16B	C23	1+x,y,z	2.876(9)	161.1(5)	
C18	H18B	C28	1-x,1-y,1-z	2.815(6)	165.6(7)	
Res. 2						
C29	H29	N11	x,1+y,-1+z	2.612(13)	170.5(11)	
C32	H32B	H27	-1+x,y,z	2.357(12)	122.7(4)	
C33	H33B	C26A	2-x,-y,1-z	2.745(5)	152.1(4)	
C33	H33B	C27	2-x,-y,1-z	2.788(5)	139.0(5)	
C33	H33B	C30A	2-x,-y,1-z	2.870(7)	166.3(4)	
C35	H35B	C1	1-x,1-y,1-z	2.880(8)	168.8(6)	
C35	H35C	C7	1-x,1-y,1-z	2.762(8)	144.9(6)	
C39	H39B	C6A	1+x,1+y,-1+z	2.859(9)	168.2(7)	
C-H-π interactions						
C13	H13A	Cg(A)	2-x,-y,1-z	2.530(6)	167.4(5)	3.5073(15)
C16	H16B	Cg(C)	1+x,y,z	2.844(8)	170.8(5)	3.8390(16)
C33	H33B	Cg(D)	2-x,1-y,-z	2.580(6)	164.1(5)	3.5628(15)
C35	H35B	Cg(A)	1-x,1-y,1-z	2.578(9)	161.1(6)	3.5487(16)

[a]Cg(X) denotes the centroid of ring X, with the lettering as indicated in Figure 1

Table S2: Intermolecular contacts shorter than the van der Waals radii in the structure of **2a**

A	H	B	Symm. eq. B	H…B (Å)	A-H…B (°)	A…Cg (Å)
Res. 1						
C1	H1	H41	1-x,-y,1-z	2.31(2)	142.5(8)	
C6	H6A	H35C	1-x,1-y,-z	2.275(15)	172.8(6)	
C9	H9	N51	2-x,-y,1-z	2.641(12)	158.8(8)	
C13	H13A	C6A	1-x,1-y,-z	2.717(9)	154.3(2)	
C13	H13A	C7B	1-x,1-y,-z	2.707(10)	141.9(3)	
C13	H13A	C10A	1-x,1-y,-z	2.888(8)	164.3(5)	
C15	H15B	C7B	1-x,-y,-z	2.808(11)	154.6(6)	
C17	H17B	C4A	1+x,y,z	2.811(12)	175.9(9)	
Res. 2						
C26	H26A	H57A	-1+x,y,z	2.392(12)	144.4(6)	
C29	H29	N5	x,1-y,-z	2.683(11)	154.7(7)	
C33	H33B	C41	1-x,-y,1-z	2.855(9)	127.9(3)	
C33	H33B	C52A	1-x,-y,1-z	2.818(9)	143.1(2)	
C35	H35A	C41	1-x,1-y,1-z	2.78(2)	156.9(13)	
C37	H37B	C32A	-1+x,y,z	2.767(11)	158.2(10)	
C35B	H35F	C42	1-x,1-y,1-z	2.85(6)	162(4)	
Res. 3						
C43	H43	N25	x,y,z	2.576(12)	164.3(10)	
C46	H46A	N45	2-x,-y,1-z	2.694(5)	132.6(6)	
C52	H52A	C30	1-x,-y,1-z	2.840(11)	158.9(4)	
C53	H53B	C26A	1-x,-y,1-z	2.797(9)	170.2(3)	
C53	H53B	C27	1-x,-y,1-z	2.786(10)	153.3(4)	
C55	H55B	C50A	-1+x,y,z	2.798(12)	170.0(9)	
C57	H57B	C27	1-x,1-y,1-z	2.847(11)	145.8(7)	

C57	H57B	C28	1-x,1-y,1-z	2.666(11)	171.0(7)	
C1	H1	H41	1-x,-y,1-z	2.31(2)	142.5(8)	
C-H-π interactions						
C13	H13A	Cg(B)[a]	1-x,1-y,-z	2.529(10)	166.6(5)	3.4978(15)
C14	H14B	Cg(A)	1-x,-y,-z	2.754(9)	142.5(6)	3.5910(15)
C17	H17B	Cg(A)	1+x,y,z	2.984(9)	150.4(6)	3.8880(18)
C33	H33B	Cg(E)	1-x,-y,1-z	2.701(10)	153.7(4)	3.6340(16)
C35	H35B	Cg(F)	1-x,1-y,1-z	2.88(2)	144.6(10)	3.720(4)
C37	H37B	Cg(C)	-1+x, y, z	2.918(10)	152.4(6)	3.8251(19)
C53	H53B	Cg(D)	1-x,-y,1-z	2.731(10)	160.4(3)	3.6822(18)
C57	H57B	Cg(D)	1-x,1-y,1-z	2.990(11)	142.8(6)	3.8184(18)
C13	H13A	Cg(B)	1-x,1-y,-z	2.529(10)	166.6(5)	3.4978(15)
C14	H14B	Cg(A)	1-x,-y,-z	2.754(9)	142.5(6)	3.5910(15)

Table S3: Intermolecular contacts shorter than the van der Waals radii in the structure of β **-3a**

A	H	B	Symm. eq. B	H…B (Å)	A-H…B (°)	A…Cg (Å)
Res. 1						
C12	H12B	C24	x,y,1+z	2.777(9)	148.9(4)	
C6	H6B	H36C	-x,-y,1-z	2.37(1)	117.0(6)	
C12	H12A	H55B	x-1,y,z	2.36(2)	174.7(8)	
C15	H15B	H52A	x-1,y,z	2.33(2)	115(1)	
Res. 2						
C32	H32A	C35	-x,-y,-z	2.87(1)	166.8(4)	
C32	H32B	C3	x,y,z	2.843(9)	146.5(3)	
C32	H32B	C4	x,y,z	2.732(9)	153.1(5)	
C33	H33A	C7	x,y,z	2.68(1)	126.3(5)	
C32	H32A	H35B	-x,-y,-z	2.37(2))	170.6(7)	
Res. 3						
C57	H57	C19	x,y,z	2.83(1)	140.3(9)	
C52	H52B	C43	x,1/2-y,z-1/2	2.840(9)	142.1(3)	
C52	H52B	C44	x,1/2-y,z-1/2	2.707(9)	148.8(5)	
C53	H53B	C47	x,1/2-y,z-1/2	2.89(1)	134.4(5)	
C59	H59C	C46a	x,1/2-y,z+1/2	2.85(1)	162.2(8)	
C-H-π interactions						
C13	H13B	Cg(C)	x,y,1+z	2.79(1)	171.0(6)	3.779(2)
C15	H15A	Cg(C)	x,y,z	2.81(1)	149.8(9)	3.710(2)
C33	H33A	Cg(B)	x,y,z	2.97(1)	142.0(7)	3.806(2)
C33	H33B	Cg(A)	x,y,z	2.81(1)	161.9(5)	3.775(2)
C35	H35A	Cg(A)	x,y,z-1	2.77(1)	157.8(9)	3.723(2)
C53	H53A	Cg(E)	x,1/2-y,z-1/2	2.74(1)	164.1(5)	3.738(2)

C55	H55A	Cg(E)	x,1/2-y,z+1/2	2.83(1)	153.1(9)	3.755(2)
C59	H59C	Cg(F)	x,1/2-y,z+1/2	2.83(1)	133.8(8)	3.608(2)

Table S4: Intermolecular contacts shorter than the van der Waals radii in the structure of γ **-3a**

A	H	B	Symm. eq. B	H…B (Å)	A-H…B (°)	A…Cg (Å)
Res. 1						
C13	H13A	C1	x,1/2-y,1/2+z	2.879(7)	129.5(3)	
C6	H6A	C9	x,1/2-y,1/2+z	2.886(6)	142.0(3)	
C6	H6A	C10	x,1/2-y,1/2+z	2.744(6)	150.8(3)	
C14B	C16B	C16B	1-x,1-y,-z	2.224(9)	150	
C16A	H16A	C12A	x,1/2-y,z-1/2	2.89	134	
C16C	H16H	H3	1-x,y-1/2,1/2-z	2.17	175	
C6	H6B	H18C	-x,1-y,-z	2.35(1)	174.0(5)	
C12	H12A	H19C	-x,y-1/2,1/2-z	2.39(1)	116.0(5)	
	H16D	C16B	1-x,1-y,-z	2.18		
	H16E	C16B	1-x,1-y,-z	2.10		
	H16F	C16B	1-x,1-y,-z	2.04		
	H16D	H16E	1-x,1-y,-z	1.90		
	H16F	H16D	1-x,1-y,-z	1.84		
	H16E	H16E	1-x,1-y,-z	2.39		
	H16E	H16F	1-x,1-y,-z	174		
	H16F	H16F	1-x,1-y,-z	2.29		
C-H-π interactions						
C13	H13B	Cg(B)	x,1/2-y,1/2+z	2.777(7)	166.3(4)	3.772(2)
C18	H18A	Cg(B)	x,1/2-y,z-1/2	2.789(7)	153.7(6)	3.721(2)
C16C	H16I	Cg(A)	x,1/2-y,z-1/2	2.80	139	3.578(2)

Table S5: Intermolecular contacts shorter than the van der Waals radii in the structure of **4a**

A	H	B	Symm. eq. B	H…B (Å)	A-H…B (°)	A…Cg (Å)
C6	H6B	C9	x,1/2-y,1/2+z	2.730(9)	153.2(4)	
C6	H6B	C10	x,1/2-y,1/2+z	2.719(9)	158.3(6)	
C13	H13A	C1	x,1/2-y,1/2+z	2.89(1)	129.0(5)	
C17	H17B	C12A	x,1/2-y,-1/2+z	2.89(1)	169.6(8)	
C19	H19A	C7	x,1/2-y,-1/2+z	2.88(1)	172.6(9)	
C20	H20C	C4	-x,-y,-z	2.87(1)	174(1)	
C20	H20C	H6A	-x,-y,-z	2.38(1)	110.3(8)	
C21	H21B	H12B	-x,-1/2+y,1/2-z	2.32(2)	128.2(8)	
C-H-π interactions						
C13	H13B	Cg(B)	x,1/2-y,1/2+z	2.96(1)	160.0(3)	3.922(2)
C15	H15A	Cg(A)	x,1/2-y,-1/2+z	2.95(1)	159(1)	3.933(2)

Table S6: Intermolecular contacts shorter than the van der Waals radii in the structure of **4b**

A	H	B	Symm. eq. B	H…B (Å)	A-H…B (°)	A…Cg (Å)
Res. 1						
C12	H12B	C4	x,1+y,z	2.828(13)	171.5(8)	
C13	H13A	C32	1/2+x,1/2+y,z	2.874(18)	147.9(3)	
C17	H17A	C31	x,y,z	2.86(2)	162.6(8)	
Res. 2						
C34	H34	C42	x,1+y,z	2.85(2)	152.8(6)	
C34	H34	H42B	x,1+y,z	2.31(2)	155.4(10)	
C36	H36A	H42A	x,1+y,z	2.215(16)	139.5(9)	
C37	H37	H40	x,1+y,z	2.31(3)	145.6(5)	
C43	H43B	C8	-1/2+x,-1/2+y,z	2.835(11)	146.4(4)	
C47	H47A	C3	1/2-x,-1/2+y,1-z	2.66(3)	162(2)	

C-H-π interactions

C13	H13A	Cg(C)	1/2+x,1/2+y, z	2.61(2)	172.0(3)	3.648(3)
C17	H17A	Cg(C)	x,y,z	2.86(2)	166.4(13)	3.889(3)
C17	H17C	Cg(D)	x,y,z	2.756(19)	152.4(15)	3.718(3)
C43	H43B	Cg(B)	-1/2+x, 1/2+y,z	2.635(14)	174.6(3)	3.626(3)
C47	H47A	Cg(A)	1/2-x,- 1/2+y,1-z	2.86(2)	169.0(18)	3.898(4)
C49	H49C	Cg(A)	x,y,z	2.937(16)	161.3(10)	3.885(3)

Table S7: Sublimation enthalpies of the structures according to calculation with the UNI atom-atom force field

	Disorder status[a]	**ΔH_{subl} (kJ.mol^{-1})**	**$\Delta H_{subl}/Z'$ (kJ.mol^{-1})**
2a	D	-395.3	-131.8
2a	d	-393.5	-131.2
2asub	D	-130.2	-130.2
2asub	d	-121.2	-121.2
α -3a	-	-290.5	-145.3
α -3asub	D_1	-140.2	-140.2
α -3asub	D_2	-53.8	-53.8
β -3a	-	-442.5	-147.5
β -3a (a)	D	-140.2	-140.2
γ -3a (b)	d	-41.4	-41.4
4a	-	-153.7	-153.7
4b	-	-289.1	-144.6

[a]D = major disorder component, d = minor disorder component. D_1 and D_2 are used if the two components have equal population.

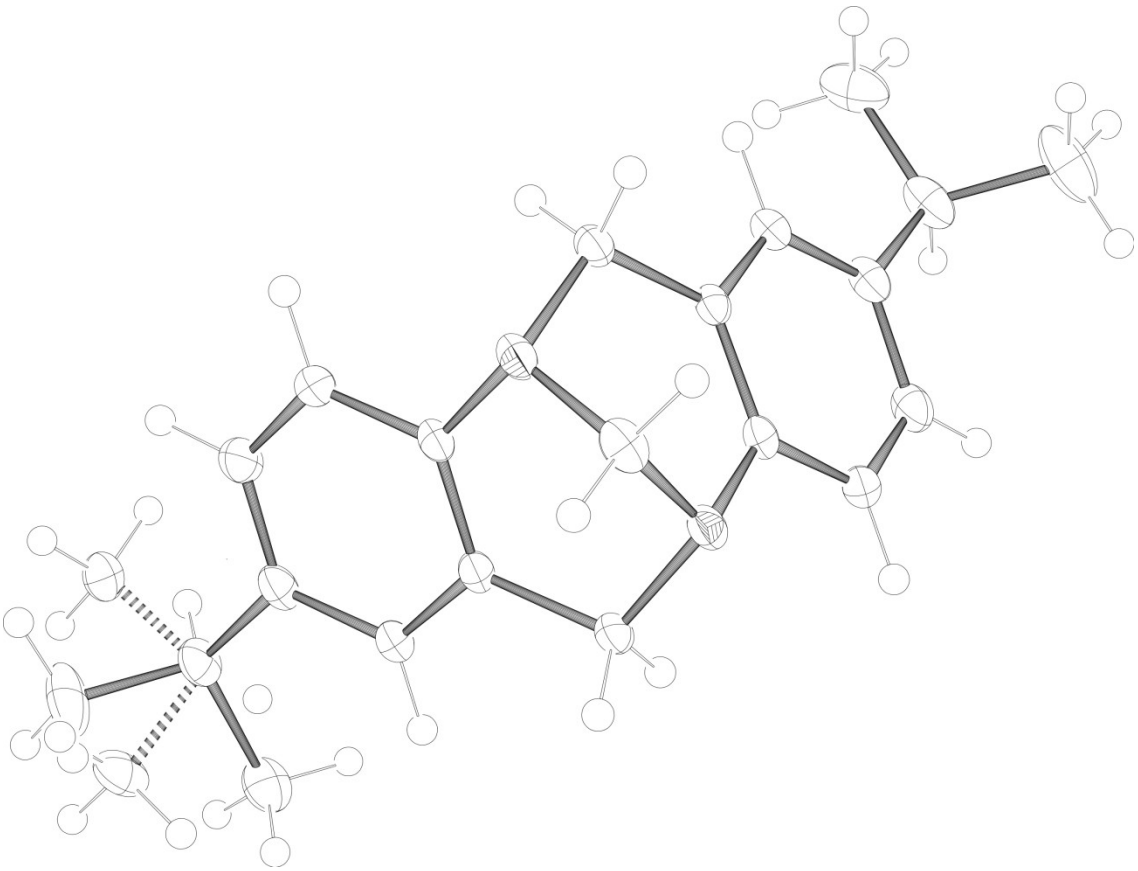

Fig S1 Displacement ellipsoid plot of **α -3a sub** at the 50% probability level. Hydrogens represented as spheres of arbitrary size. Disorder component indicated by dashed bonds.

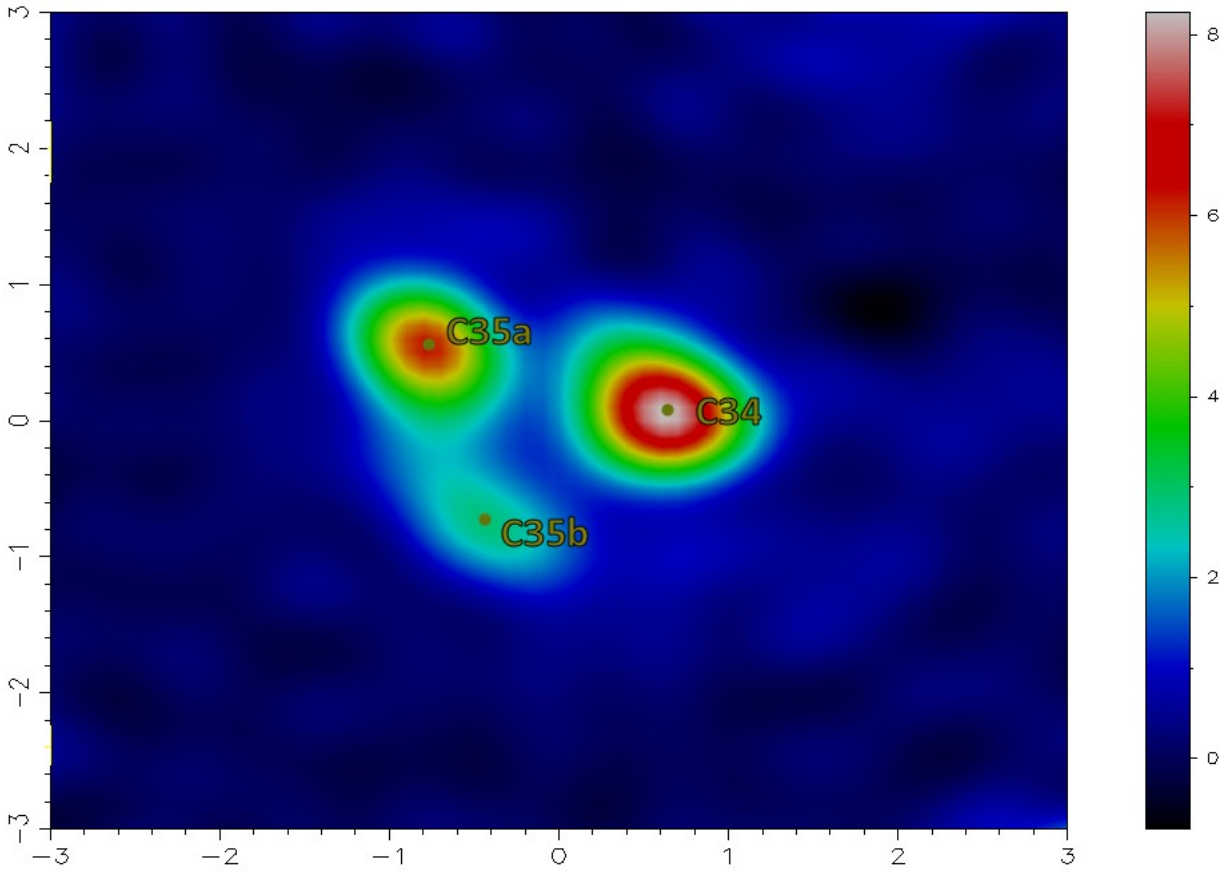

Figure S2 Fourier map through the plane of the disordered ethyl group in structure **2a**

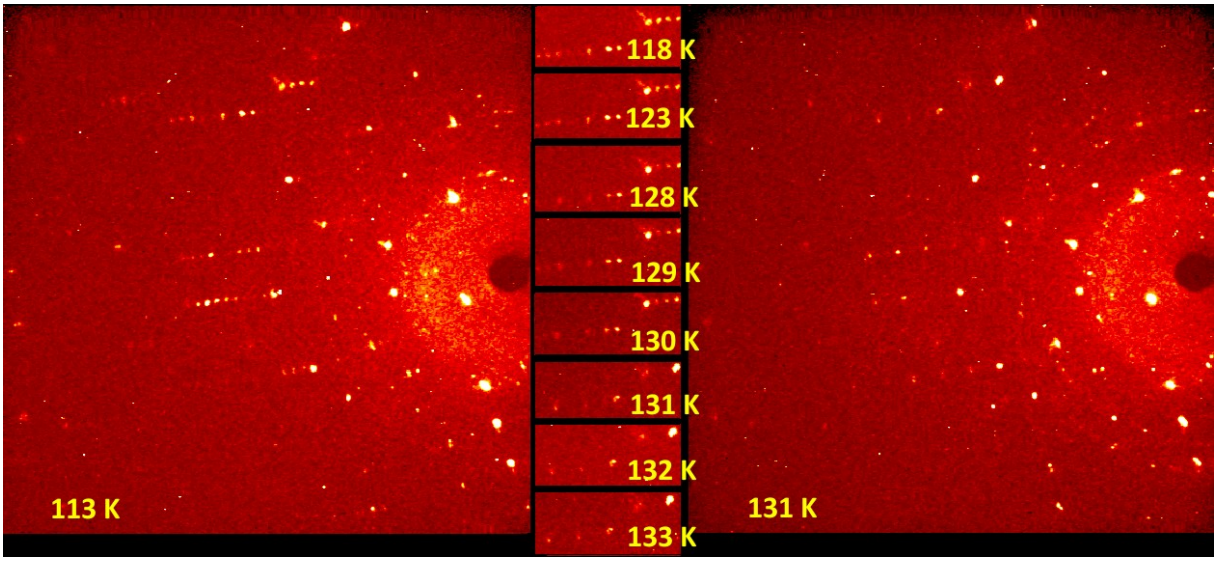

Figure S3 Frames showing the β -**3a**-γ -**3a** transition. The larger cell can be seen to (dis)appear sharply between 130-131K.