Supplementary Information

Concomitant dimorphism and helical self-assembly in a C_{2h}-symmetric 'locked' cyclitol

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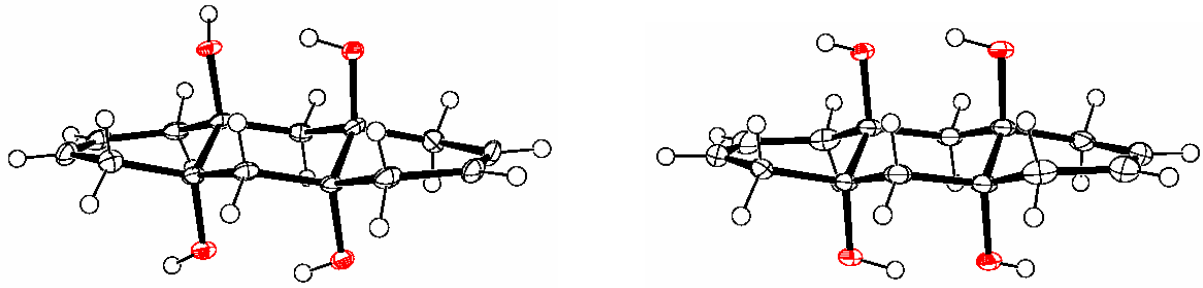
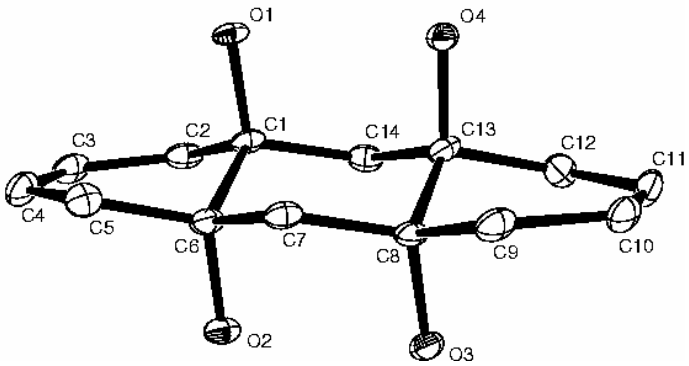
Table 1. Crystal data for the α- and β- forms of tetrol 1, and tetrol 2

	α- form	**β- form**	**2**
Molecular formula	$C_{14}H_{20}O_4$	$C_{14}H_{20}O_4$	$C_{14}H_{24}O_4$
Molecular weight	252.3	252.3	256.4
Crystal system	Tetragonal	Triclinic	Triclinic
Cell dimensions			
a (Å)	6.780 (1)	9.821 (2)	5.958(5)
b (Å)	6.780 (1)	9.926 (2)	5.994(5)
c (Å)	27.425 (7)	13.927 (3)	9.867(8)
α (^{0})	90.00	92.912 (3)	86.17(1)
β (^{o})	90.00	101.065 (3)	82.55(1)
γ (^{o})	90.00	91.848 (4)	73.20(1)
V (Å^3)	1260.74 (4)	1256.40 (9)	334.3(1)
Z	4	4	1
Space group	$P4_1$	P-1	P-1
Calc. Density (g cm^{-3})	1.33	1.33	1.27
F_{000}	543.9	543.9	140.0
μ (mm^{-1})	0.10	0.10	0.09
2θ range	3.0 – 27.3	1.5 – 25.4	2.1 – 25.4
h $_{min,max}$; k $_{min,max}$; l $_{min,max}$	-8, 8; -8, 8; -33, 34	-11, 11; -11, 11; -16, 16	-7, 7; -6, 7; -11, 11
Total no. of reflections	12972	12479	2431
Unique reflections	1450	4580	1213
No. of parameters	243	485	84
R, R_w	0.0422, 0.0986	0.0519, 0.1458	0.0504, 0.1471
GooF	1.224	1.021	1.058
$\Delta\rho_{min}$, ρ_{max} (eÅ^{-3})	-0.16, 0.25	-0.22, 0.47	-0.20, 0.32

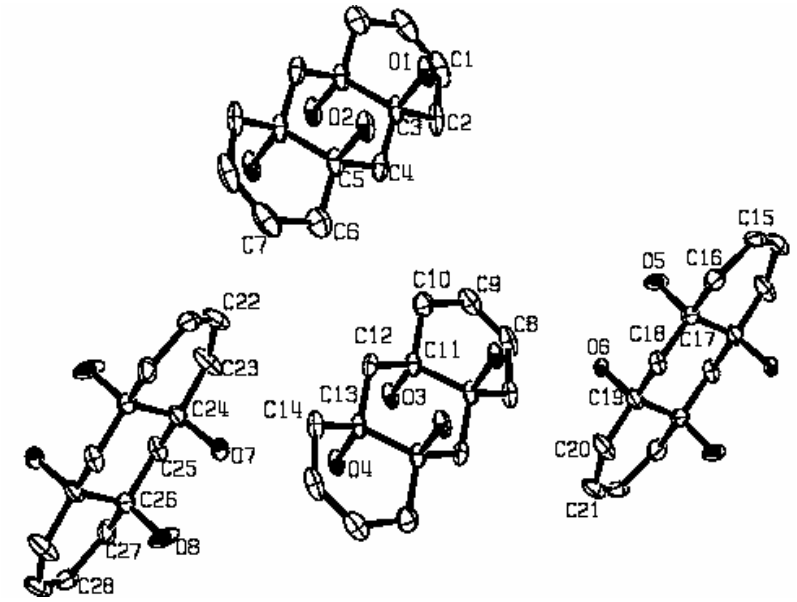
ORTEP DIAGRAMS AND ATOM NUMBERING SCHEMES



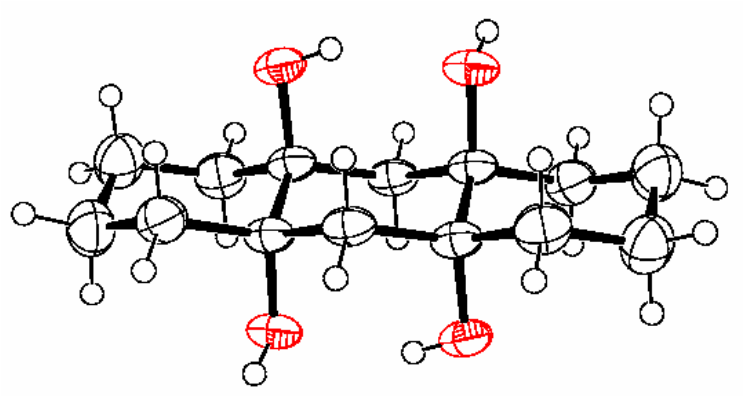
ORTEP diagrams of the α-form (*left*) and the β-form (*right*) at 100 K
with 50% ellipsoid probability



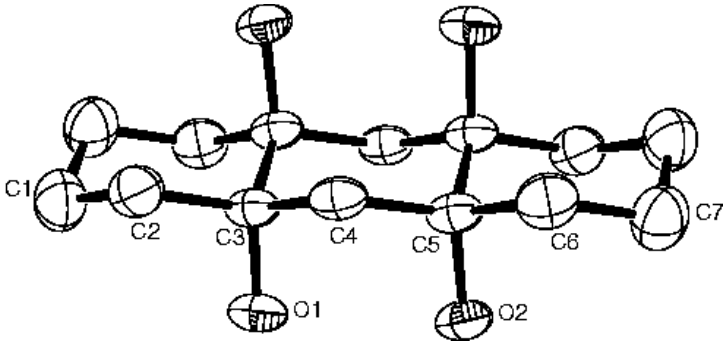
Atom numbering of the asymmetric unit in the α-form
(the hydrogen atoms have been excluded for clarity)



Atom numbering of the asymmetric unit in the β-form
(the hydrogen atoms have been excluded for clarity)



ORTEP diagrams of tetrol **2** at 292 K with 50% ellipsoid probability



Atom numbering of the asymmetric unit in tetrol **2**
(the hydrogen atoms have been excluded for clarity)

Table 2. Relevant torsion angles in the α- form

	Angle (°)	s. u.		Angle (°)	s. u.
O1 -C1 -C6 -O2	-179.67	0.14	**C14 -C1 -C2 -C3**	164.60	0.16
O1 -C1 -C6 -C7	-65.48	0.19	**O2 -C6 -C7 -C8**	61.68	0.20
O1 -C1 -C6 -C5	58.50	0.19	**C1 -C6 -C7 -C8**	-55.52	0.21
C14 -C1 -C6 -O2	-61.64	0.20	**C5 -C6 -C7 -C8**	-178.93	0.16
C14 -C1 -C6 -C7	52.56	0.21	**O2 -C6 -C5 -C4**	-73.49	0.21
C14 -C1 -C6 -C5	176.53	0.16	**C1 -C6 -C5 -C4**	47.62	0.22
C2 -C1 -C6 -O2	62.22	0.20	**C7 -C6 -C5 -C4**	170.74	0.16
C2 -C1 -C6 -C7	176.41	0.16	**C1 -C14 -C13 -O4**	-63.85	0.20
C2 -C1 -C6 -C5	-59.62	0.21	**C1 -C14 -C13 -C12**	178.19	0.16
O1 -C1 -C14 -C13	59.99	0.20	**C1 -C14 -C13 -C8**	55.30	0.21
C2 -C1 -C14 -C13	-177.47	0.16	**C6 -C7 -C8 -C13**	56.29	0.21
O1 -C1 -C2 -C3	-73.07	0.20	**C6 -C7 -C8 -C9**	179.02	0.16
C6 -C1 -C2 -C3	41.42	0.22	**O4 -C13 -C12 -C11**	72.60	0.21
C5 -C4 -C3 -C2	0.95	0.32	**C14 -C13 -C12 -C11**	-167.66	0.17
C4 -C3 -C2 -C1	-13.09	0.29	**C8 -C13 -C12 -C11**	-44.76	0.23
C12 -C11 -C10 -C9	-1.97	0.34	**O4 -C13 -C8 -O3**	-173.32	0.14
C12 -C13 -C8 -C9	58.87	0.20	**O4 -C13 -C8 -C7**	65.83	0.19
C10 -C9 -C8 -O3	72.84	0.20	**O4 -C13 -C8 -C9**	-57.25	0.19
C10 -C9 -C8 -C7	-166.33	0.17	**C14 -C13 -C8 -O3**	66.90	0.19
C10 -C9 -C8 -C13	-43.96	0.22	**C14 -C13 -C8 -C7**	-53.95	0.20
C8 -C9 -C10 -C11	16.12	0.29	**C14 -C13 -C8 -C9**	-177.03	0.16
C6 -C5 -C4 -C3	-18.87	0.28	**C12 -C13 -C8 -O3**	-57.19	0.20
C13 -C12 -C11 -C10	17.13	0.30	**C12 -C13 -C8 -C7**	-178.05	0.16

Table 3. Relevant torsion angles in the β- form

	Angle (°)	s. u.		Angle (°)	s. u.
C3 -C4 -C5 -O2	-62.72	0.19	**C11 -C12 -C13 -O4**	-60.26	0.19
C3 -C4 -C5 -C6	177.86	0.16	**C11 -C12 -C13 -C14**	177.80	0.15
C5 -C4 -C3 -O1	64.17	0.20	**C13 -C12 -C11 -O3**	63.82	0.19
C5 -C4 -C3 -C2	-177.60	0.16	**C13 -C12 -C11 -C10**	-177.99	0.15
C19 -C18 -C17 -O5	61.10	0.21	**C9 -C10 -C11 -O3**	-69.55	0.19
C19 -C18 -C17 -C16	-178.74	0.17	**C9 -C10 -C11 -C12**	170.48	0.16
C17 -C18 -C19 -O6	-58.15	0.21	**C11 -C10 -C9 -C8**	-19.27	0.28
C17 -C18 -C19 -C20	178.17	0.17	**C26 -C25 -C24 -O7**	63.62	0.21
O5 -C17 -C16 -C15	-69.23	0.22	**C26 -C25 -C24 -C23**	-178.24	0.17
C18 -C17 -C16 -C15	168.95	0.18	**C24 -C25 -C26 -O8**	-58.81	0.21
C7 -C6 -C5 -O2	72.77	0.22	**C24 -C25 -C26 -C27**	179.55	0.16
C7 -C6 -C5 -C4	-171.20	0.18	**C28 -C27 -C26 -O8**	71.51	0.23
C1 -C2 -C3 -O1	-75.02	0.20	**C28 -C27 -C26 -C25**	-169.81	0.18
C1 -C2 -C3 -C4	164.40	0.17	**C25 -C24 -C23 -C22**	164.32	0.19
O6 -C19 -C20 -C21	71.80	0.23	**C18 -C19 -C20 -C21**	-165.29	0.18

Table 4. Relevant torsion angles in the tetrol 2

				Angle (^{o})	s. u.
C5	**-C4**	**-C3**	**-O1**	61.45	0.17
C5	**-C4**	**-C3**	**-C2**	-179.14	0.14
C3	**-C4**	**-C5**	**-O2**	-61.72	0.17
C3	**-C4**	**-C5**	**-C6**	179.04	0.14
O1	**-C3**	**-C2**	**-C1**	-59.94	0.19
C4	**-C3**	**-C2**	**-C1**	179.57	0.15
O2	**-C5**	**-C6**	**-O7**	58.84	0.19
C4	**-C5**	**-C6**	**-C7**	179.39	0.15

Table 5. Intra- and Intermolecular interactions in the α- form

D-H...A	D-H (Å)	D...A (Å)	H...A (Å)	∠D-H...A (°)	Symmetry
O3-H3O...O2	0.80 (3)	2.602 (2)	1.88 (3)	149 (3)	x, y, z
O4-H4O...O1	0.81 (3)	2.690 (2)	1.95 (3)	152 (2)	x, y, z
O2-H2O...O4	0.87 (3)	2.702 (2)	1.84 (3)	167 (2)	x + 1, y, z
O1-H1O...O3	0.92 (3)	2.722 (2)	1.82 (3)	167 (3)	-y, x, z + ¼
C10-H10...O1	0.94 (3)	3.551 (2)	2.71 (3)	149 (2)	y - 1,-x, z - ¼
C9-H9A...O2	0.94 (2)	3.382 (3)	2.79 (2)	123 (2)	x - 1, y, z
C2-H2B...O4	0.91 (2)	3.320 (2)	2.78 (2)	119 (2)	x + 1, y, z

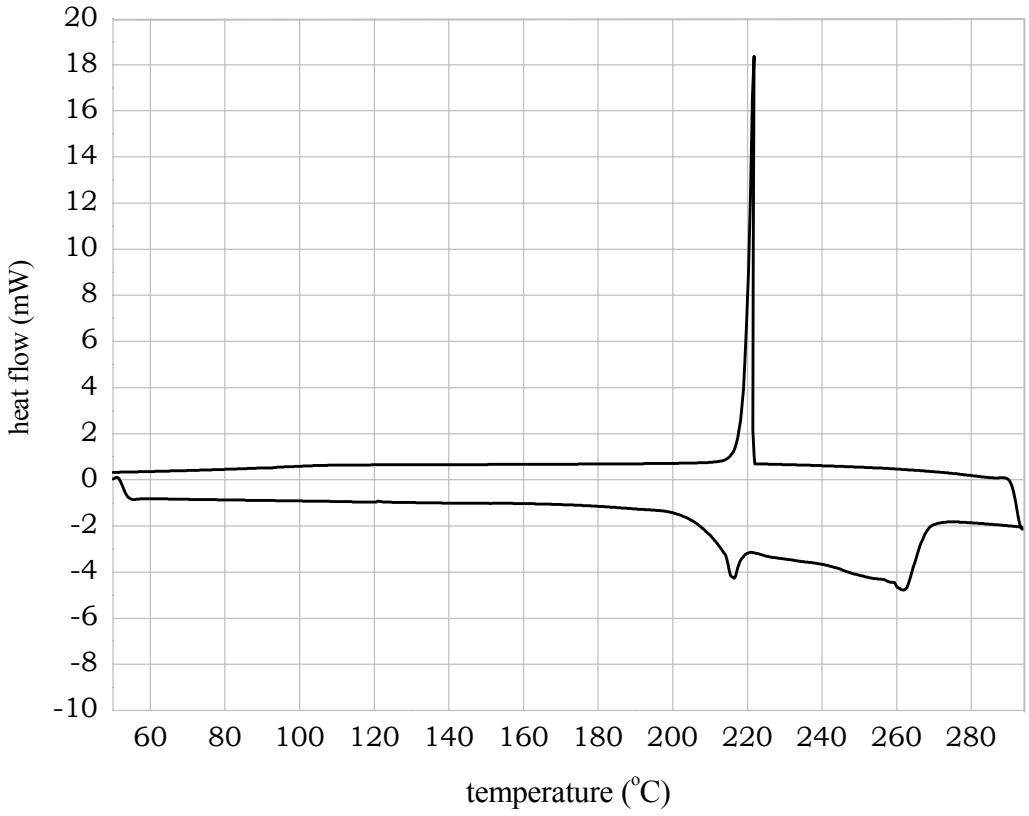
Table 6. Intra- and Intermolecular interactions in the β- form

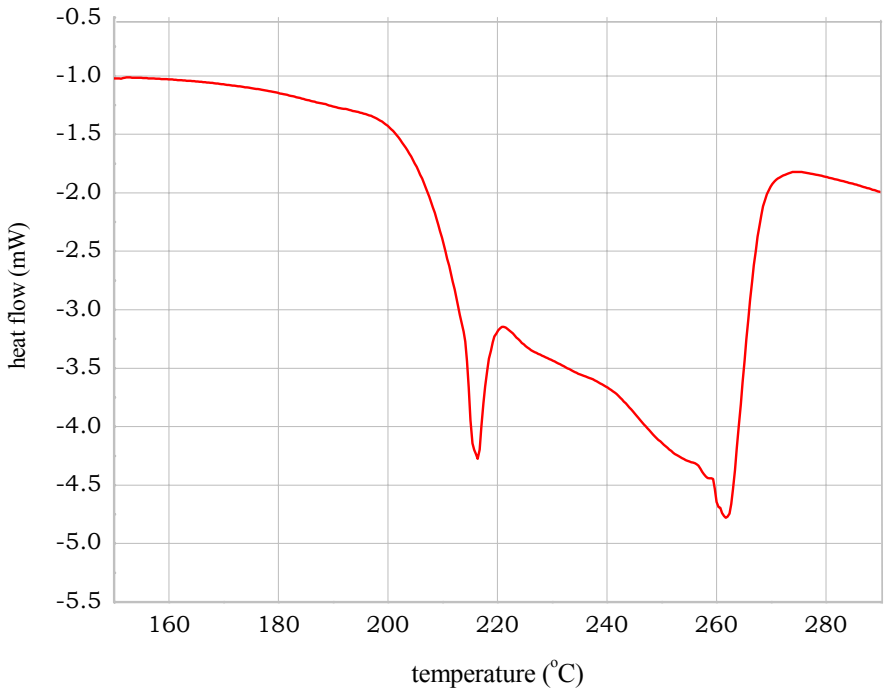
D-H...A	D-H (Å)	D...A (Å)	H...A (Å)	∠D-H...A (°)	Symmetry
O1-H1O...O2	0.85 (2)	2.630 (2)	1.85 (2)	152 (2)	x, y, z
O5-H5O...O6	0.84 (3)	2.641 (2)	1.87 (3)	152 (3)	x, y, z
O3-H3O...O4	0.82 (2)	2.682 (2)	1.94 (2)	150 (2)	x, y, z
O7-H7O...O8	0.87 (3)	2.595 (2)	1.80 (3)	150 (3)	x, y, z
O4-H4O...O7	0.89 (3)	2.747 (2)	1.87 (3)	169 (2)	x, y, z
O2-H2O...O3	0.73 (2)	2.801(2)	2.09 (2)	167 (2)	x, y+1, z
O8-H8O...O5	0.82 (3)	2.576 (3)	1.77 (3)	169 (3)	x + 1, y, z + 1
O6-H6O...O1	0.85 (3)	2.734 (2)	1.90 (3)	168 (3)	x, y - 1, z
C14-H14A...O2	0.94 (2)	3.248 (3)	2.57 (2)	129 (2)	-x + 2, -y + 2, -z + 1
C2-H2B...O3	0.98 (2)	3.172 (3)	2.49 (2)	126 (2)	-x + 1, -y + 1, -z + 1
C14-H14B...O7	1.00 (2)	3.465 (3)	2.70 (2)	133 (1)	x, y, z
C2-H2A...O6	1.00 (2)	3.398 (3)	2.65 (2)	131 (2)	x, y + 1, z

Table 7. Intra- and Intermolecular interactions in tetrol 2

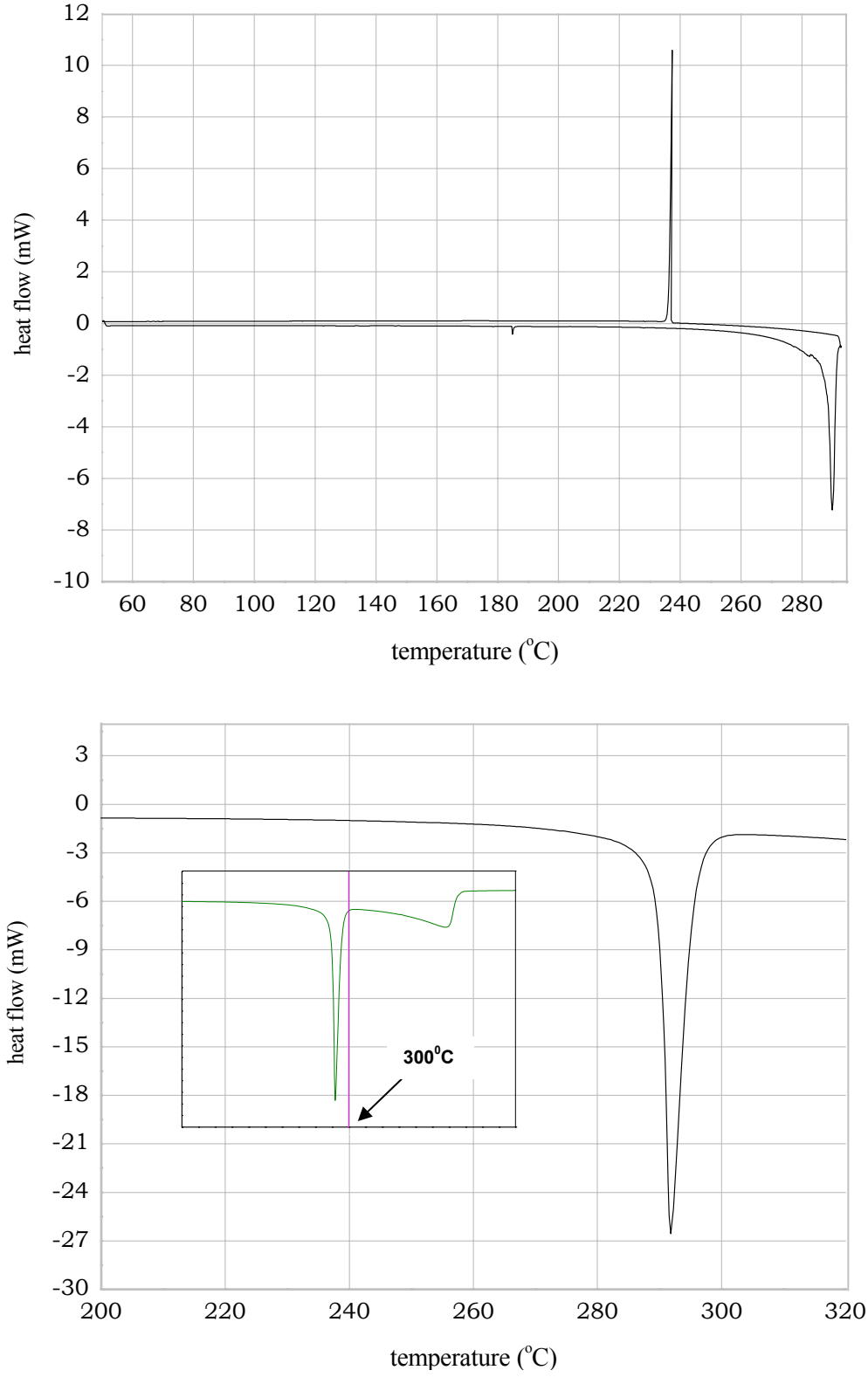
D-H...A	D-H (Å)	D...A (Å)	H...A (Å)	∠D-H...A (°)	Symmetry
O2-H2...O1	0.82	2.670 (3)	1.94	148	x, y, z
O1-H1...O2	0.82	2.814 (3)	2.01	167	-x, -y, -z + 1

DSC characteristics



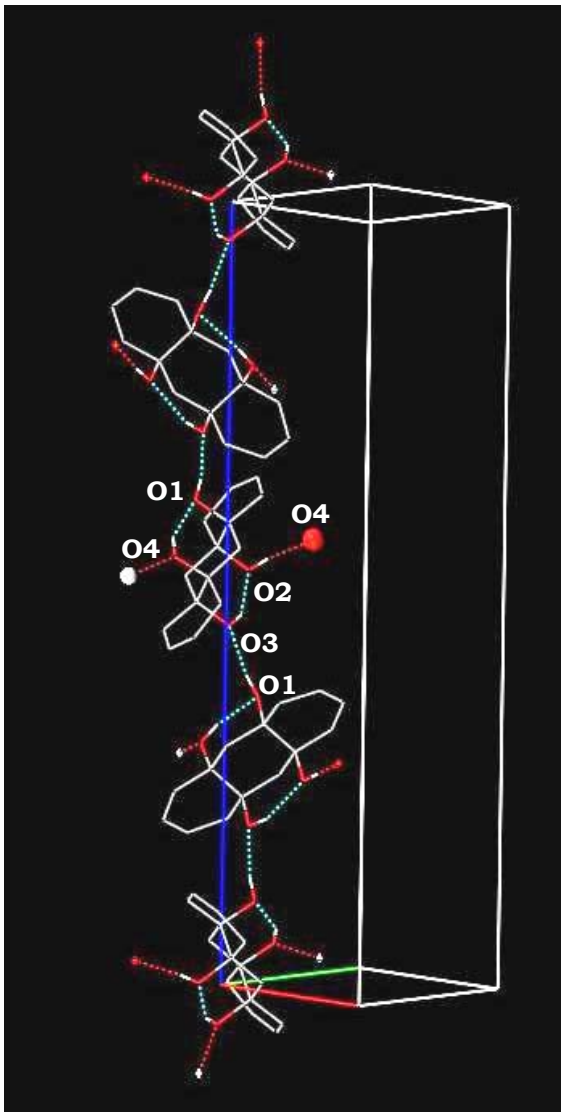


DSC plots for the α- form, showing the heating and cooling curves (*top*). A magnified view of the unique melting endotherm has also been shown (*bottom*); the enthalpy change for the transition = - 51.52 $kJmol^{-1}$.

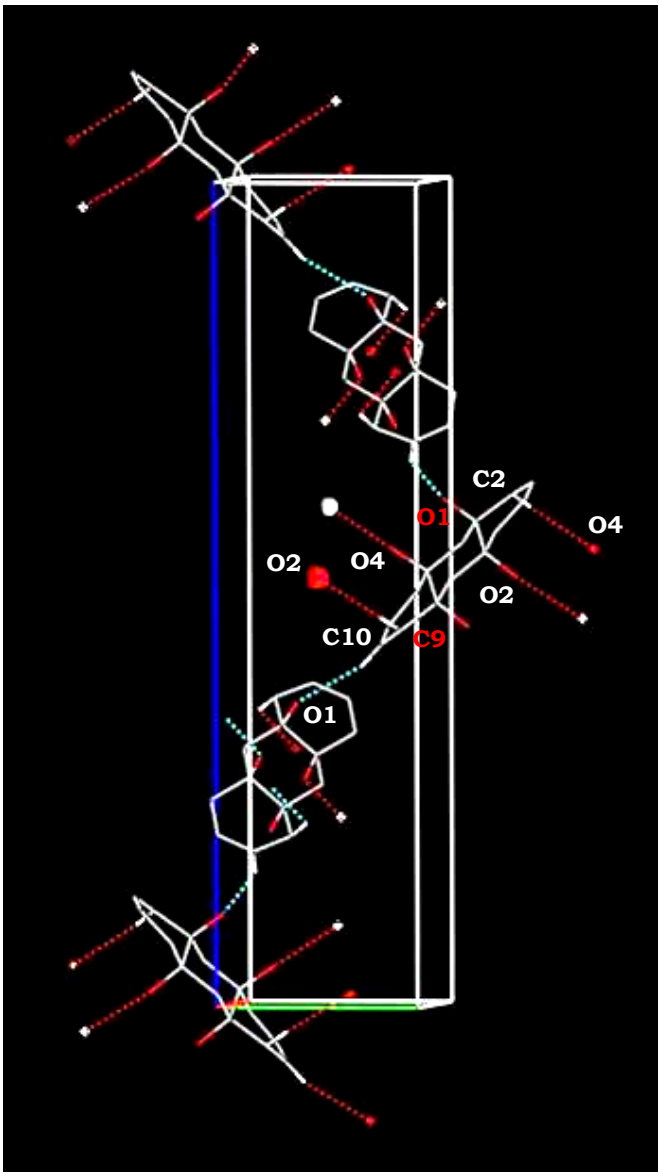


DSC plots for the b-form, showing the heating and cooling curves (*top*). The compound decomposes on melting (*inset, bottom*), so that to determine the enthalpy of transition, a single heating run (*bottom*) was performed. The enthalpy change corresponds to - 40.08 $kJmol^{-1}$.

Packing diagrams of the α-form

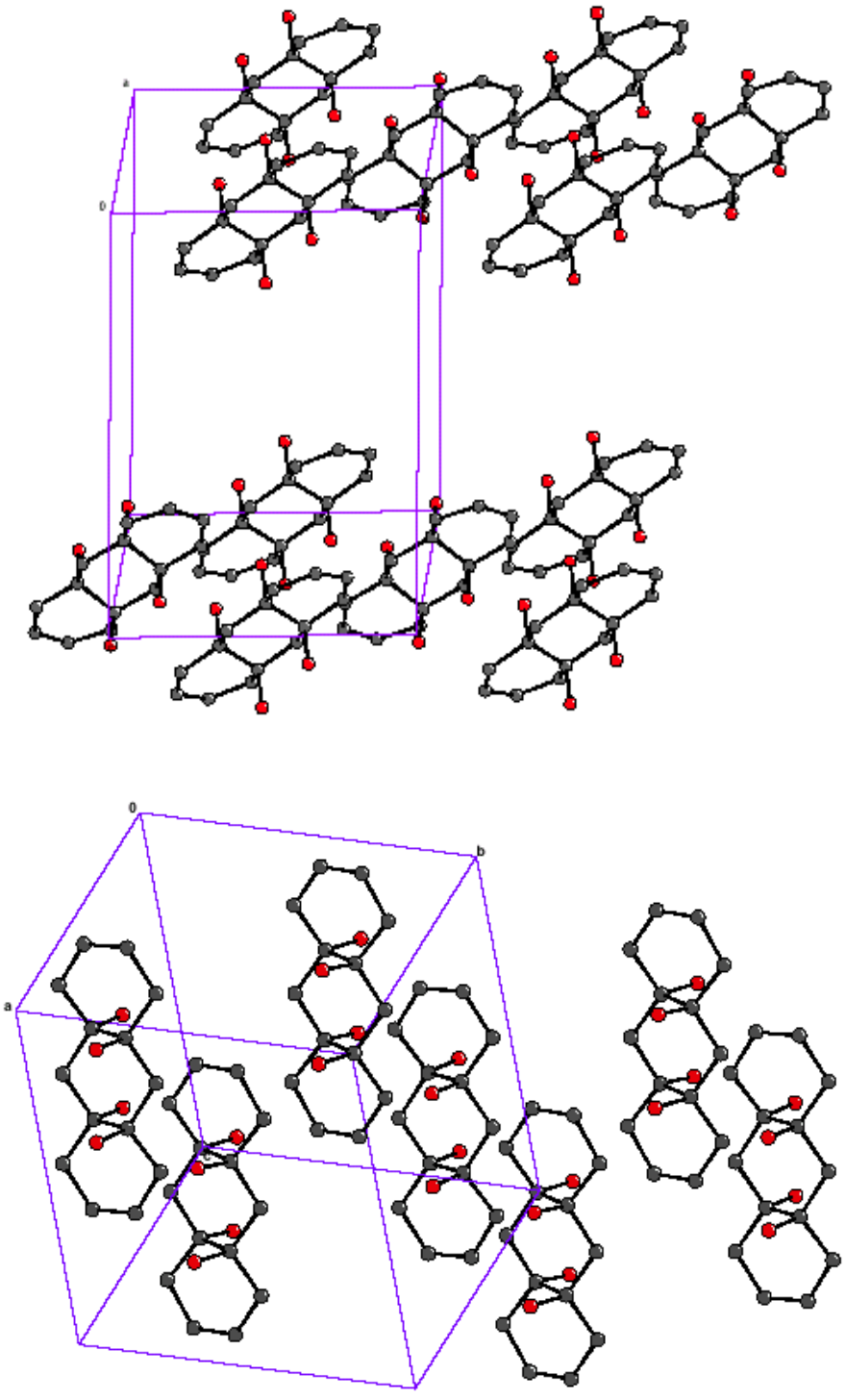


The O-H...O hydrogen bonded helical assembly. The non-interacting hydrogen atoms have been removed for clarity.

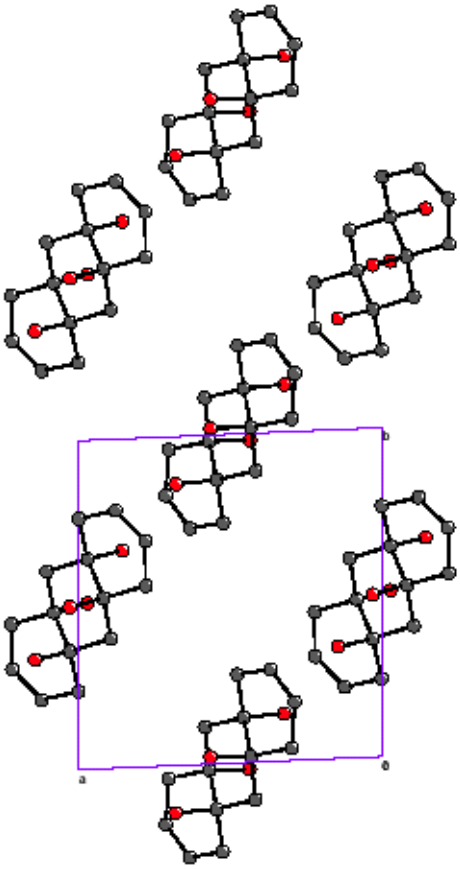


The helical assembly mediated by C-H...O intermolecular interactions. The non-interacting hydrogen atoms have been removed for clarity.

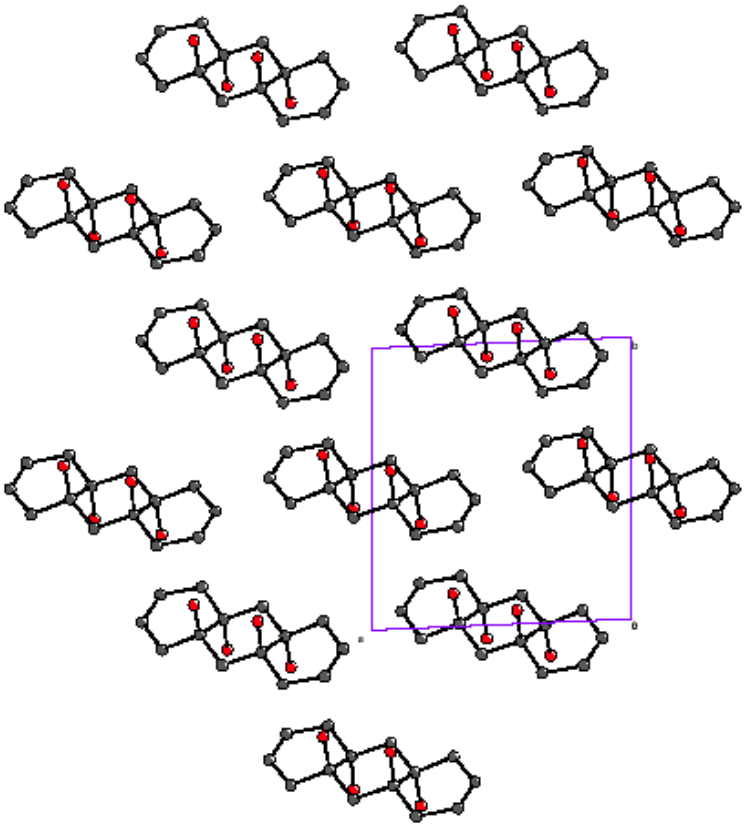
Packing diagrams of the β-form



Molecular packing diagram of the β- form, showing the arrangement of the A- (*top*) and B-type molecules (*bottom*) in the unit cell. Note that the centroids of the A-type molecules lie at (0.5, 0, 0) and (0, 0.5, 0), while those of the B-type lie at (0, 0.5, 0.5) and (0.5, 0, 0.5), so that the two sets of molecules are organized in two layers parallel to the *ab* plane. The hydrogen atoms have been removed for clarity.

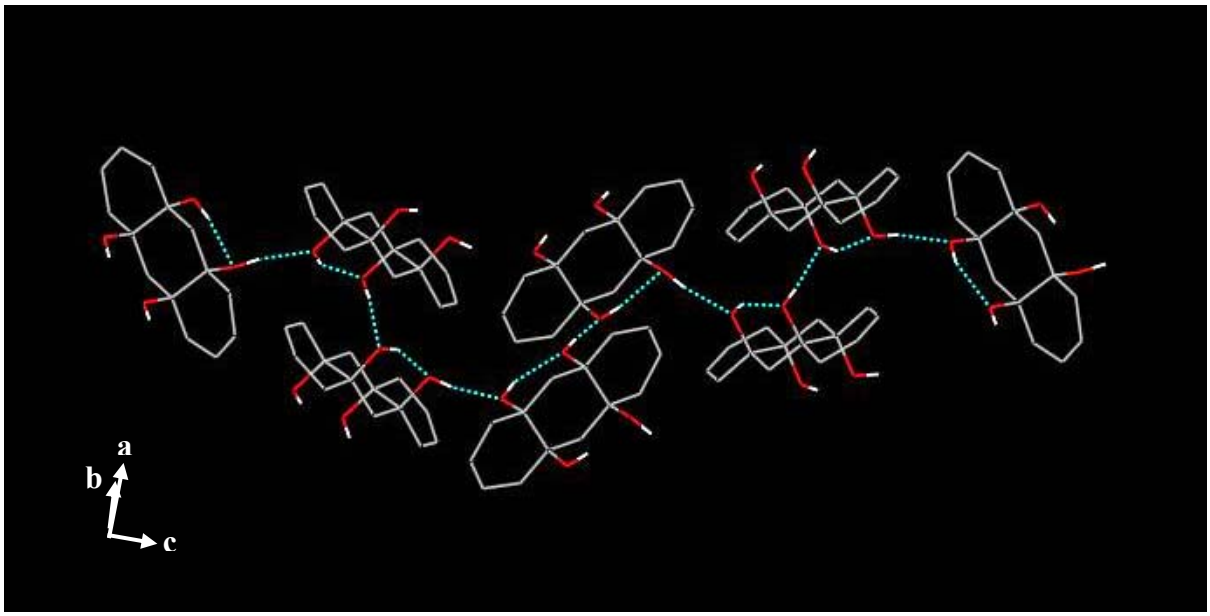


Molecular packing diagram of the β- form, showing the organization of the A-type molecules as seen down the *c*-direction. The hydrogen atoms have been removed for clarity.

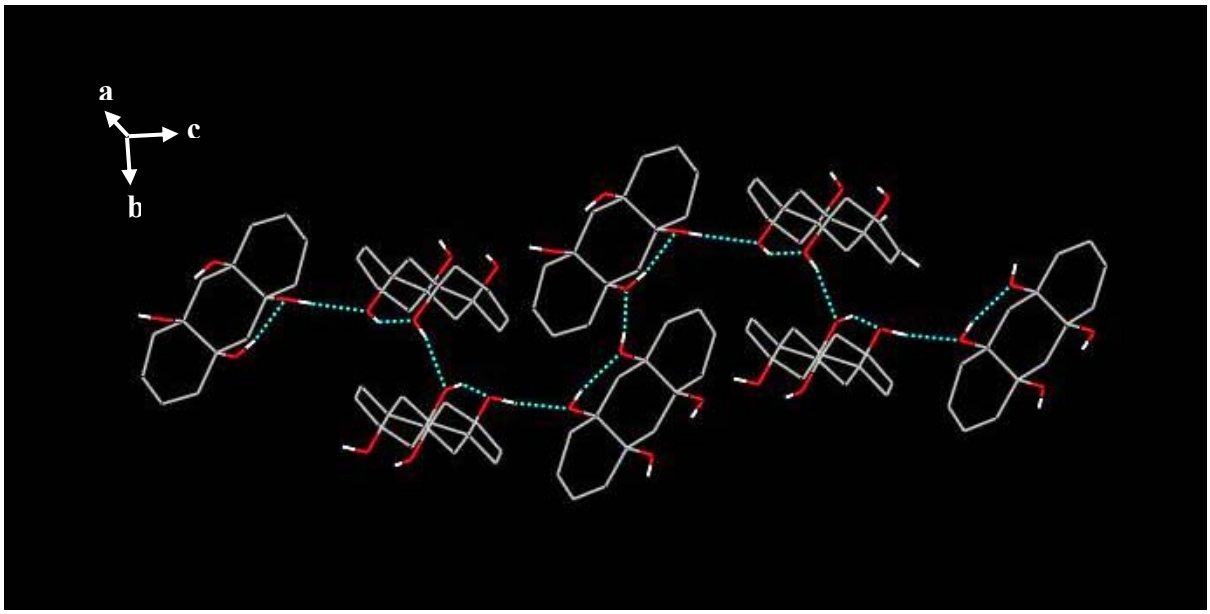


Molecular packing diagram of the β- form, showing the organization of the B-type molecules as seen down the *c*-direction. The hydrogen atoms have been removed for clarity.

Comparison of the cooperative hydrogen bonding networks in the dimorphs of 1



The cooperative hydrogen bonding network in the α-form of **1**



The cooperative hydrogen bonding network in the β-form of **1**