Electronic Supplementary Material (ESI) for CrystEngComm.

Is "configurational polymorphism" a valid concept? Structures of two forms of 4-hydroxypiperidine with different NH configurations

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Supplementary Material

Compound **1** = 4-hydroxypiperidine

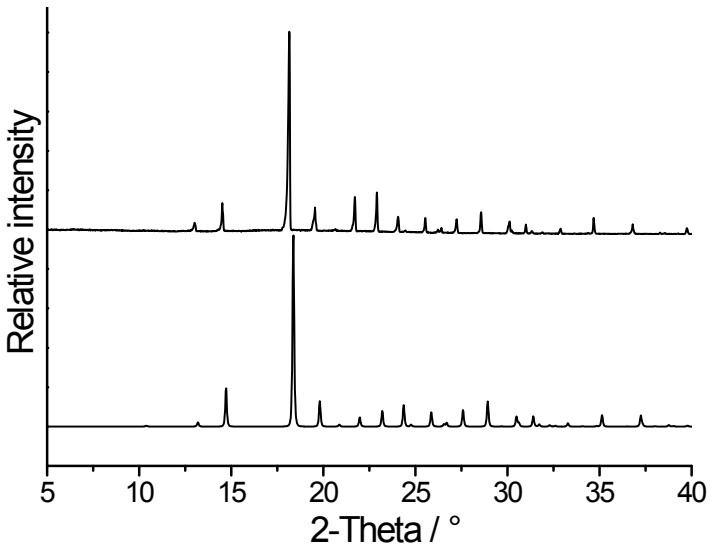

Figure S1: Experimental X-ray powder pattern of the commercial available compound **1** (top) and calculated powder pattern for form **1t** (bottom).

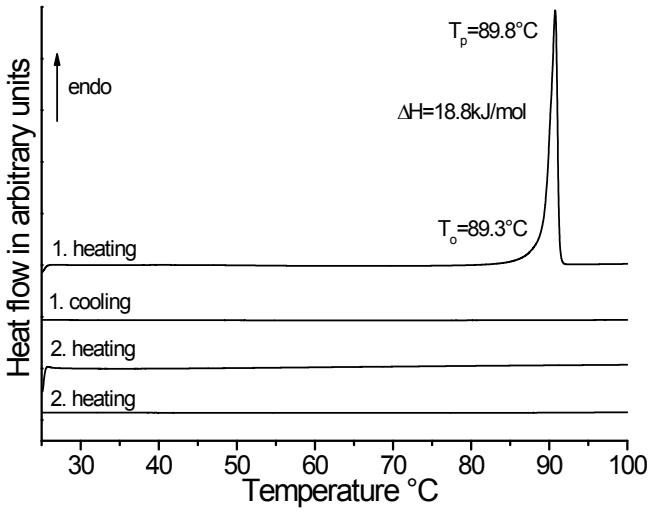

Figure S2: DSC heating and cooling curves for form **1t** at 3°C/min; given are the peak (T_p) and onset (T_o) temperatures in °C and the enthalpy ΔH in kJ/mol.

Table S1: Melting temperatures and enthalpy of fusion for various DSC runs measured at 10°C/min.

Run	Onset temperature (T_o)	Peak temperature (T_o)	Heat of fusion
1	89.5	90.3 °C	17.5 kJ/mol
2	89.3	90.1°C	19.1 kJ/mol
3	89.7	90.5 °C	18.5 kJ/mol
4	89.6	90.4 °C	18.1 kJ/mol
Average	89.5 °C	90.3 °C	18.3 kJ/mol

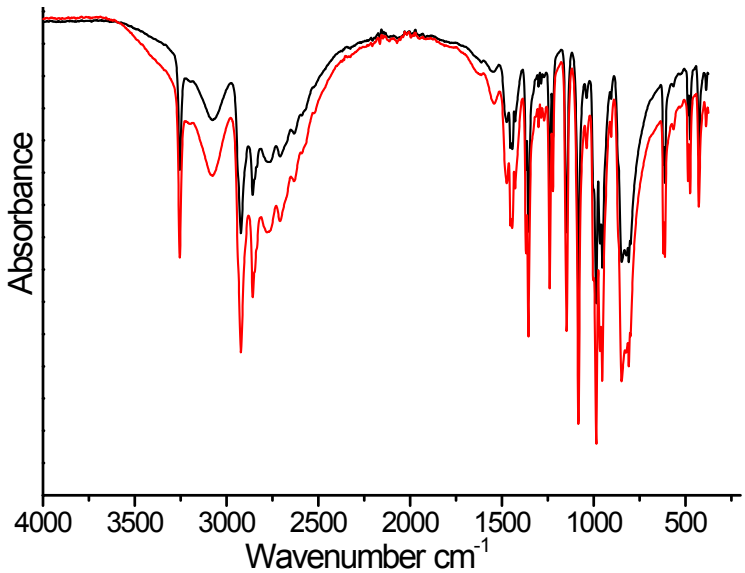

Figure S3: IR spectra of form **1t** (black) and the amorphous residue obtained after cooling the melt of form **1t** (red).

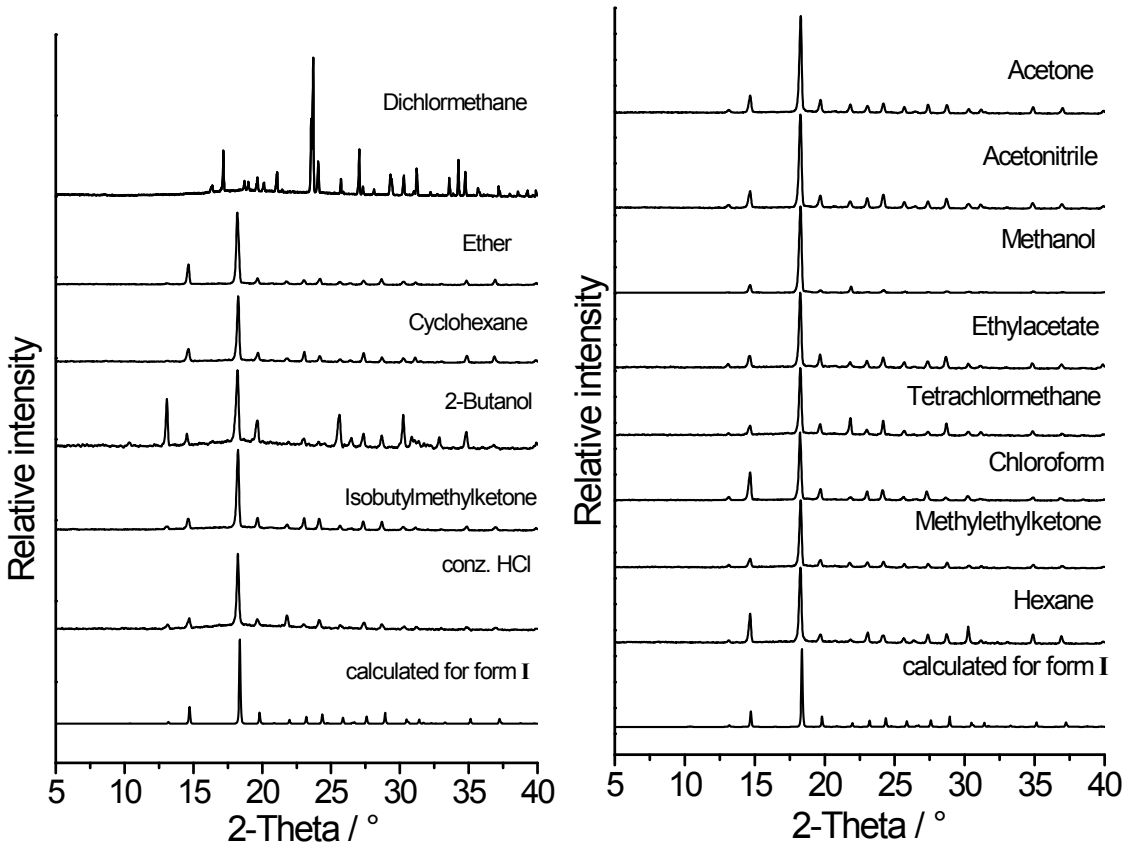

Figure S4: X-ray powder patterns of the residues of **1** obtained from various solvents. Some of these patterns show a marked texture.

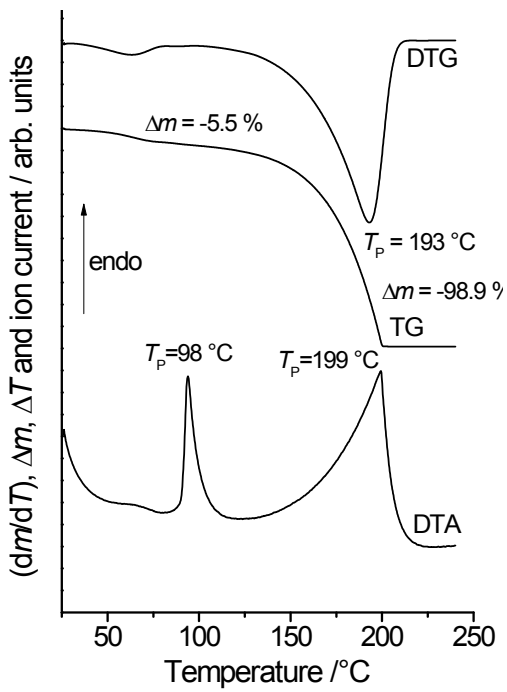

Figure S5: DTA, TG and DTG curves for the residue of **1** obtained from 2-butanol.

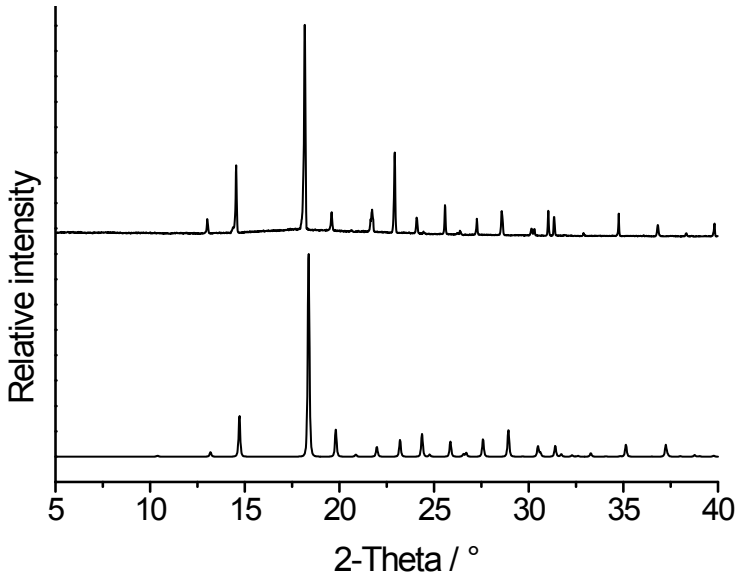

Figure S6: Experimental X-ray powder pattern of the residue obtained after solvent removal from the 2-butanol solvate (top) and calculated powder pattern for form **1t** (bottom).

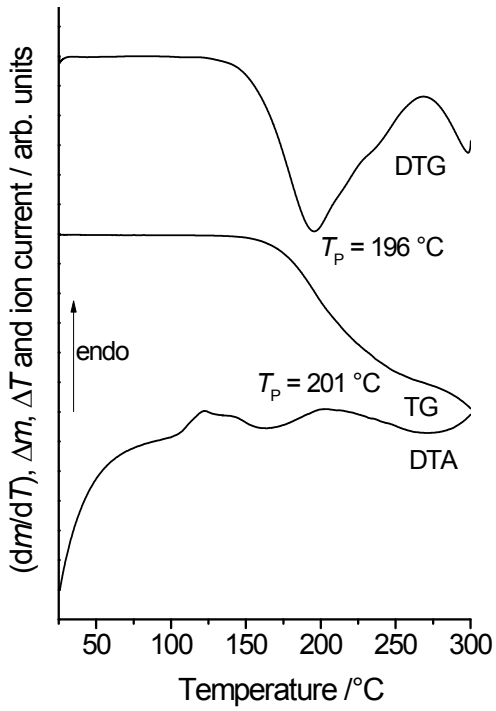

Figure S7: DTA, TG and DTG curve for the hydrochloride of 4-hydroxypiperidine.

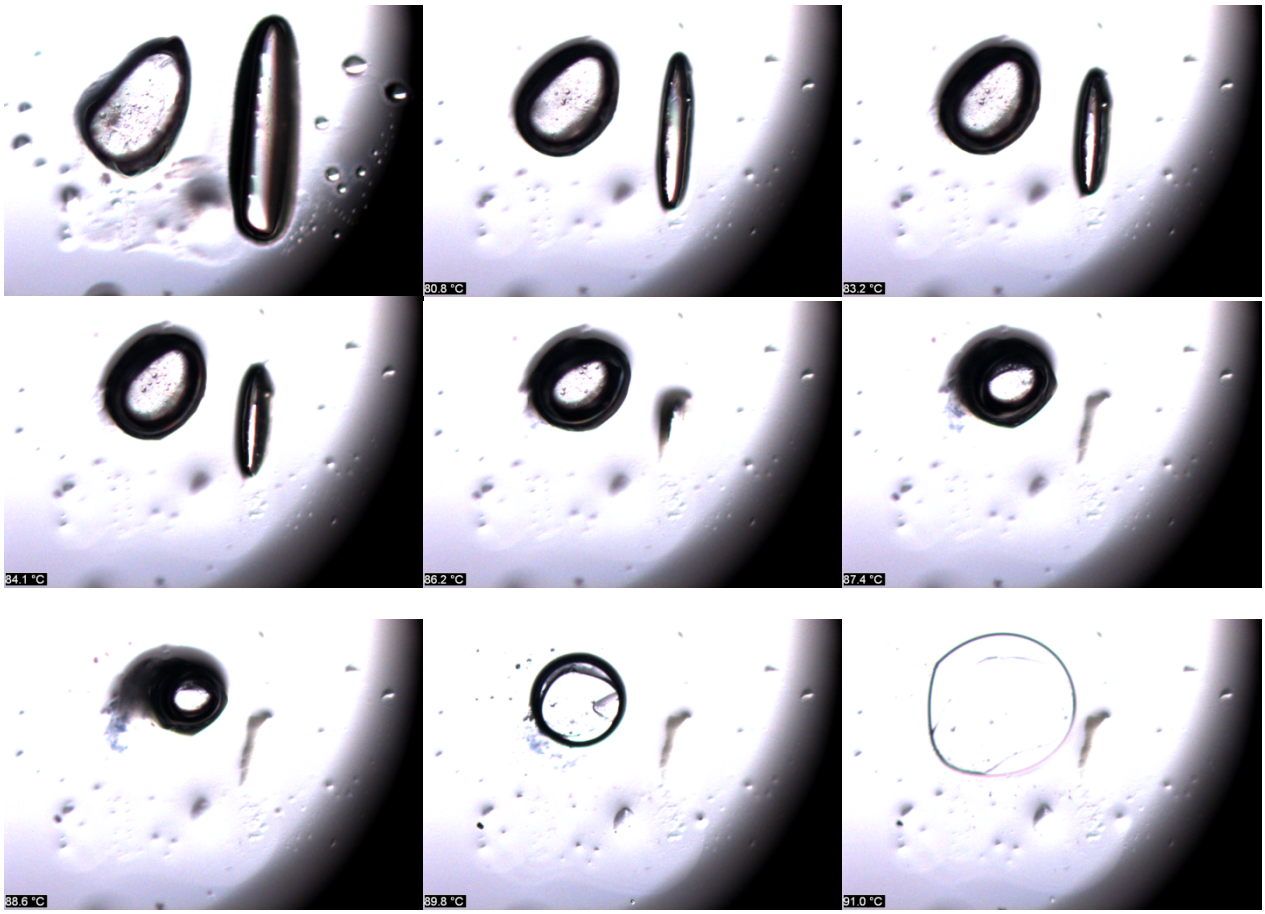

Figure S8: Microscopic images at various temperatures obtained by thermomicroscopy with form **1o** (left) and form **1t** (right).

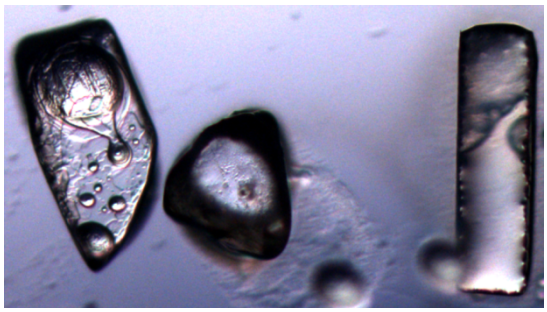

Figure S9: Microscopic images of selected crystals of **2** (left), **1o** (centre) and **1t** (right).

Packing analyses of compounds 2, 3 and 4

Compound 2

All three classical H bond donors are involved in H bonds with the chloride as acceptor (Table S2, Fig. S10). The extended packing is a layer structure parallel to the *ac* plane. Each layer involves only translation symmetry, and there are thus four layers per cell (at $y \approx 1/8, 3/8, 5/8, 7/8$). The layers consist of rings with the graph set $R_6^3(20)$.

Table S2. Classical hydrogen bonds [Å and °] for **2**.

D–H□A	d(D–H)	d(H□A)	d(D□A)	<(DHA)
O1–H03□Cl1	0.832(18)	2.333(18)	3.1613(10)	173.6(16)
N1–H01□Cl1#1	0.880(16)	2.273(16)	3.1427(10)	169.7(14)
N1–H02□Cl1#2	0.900(16)	2.262(16)	3.1524(10)	170.2(13)

Symmetry transformations used to generate equivalent atoms:
#1 x+1, y, z–1; #2 x, y, z–1.

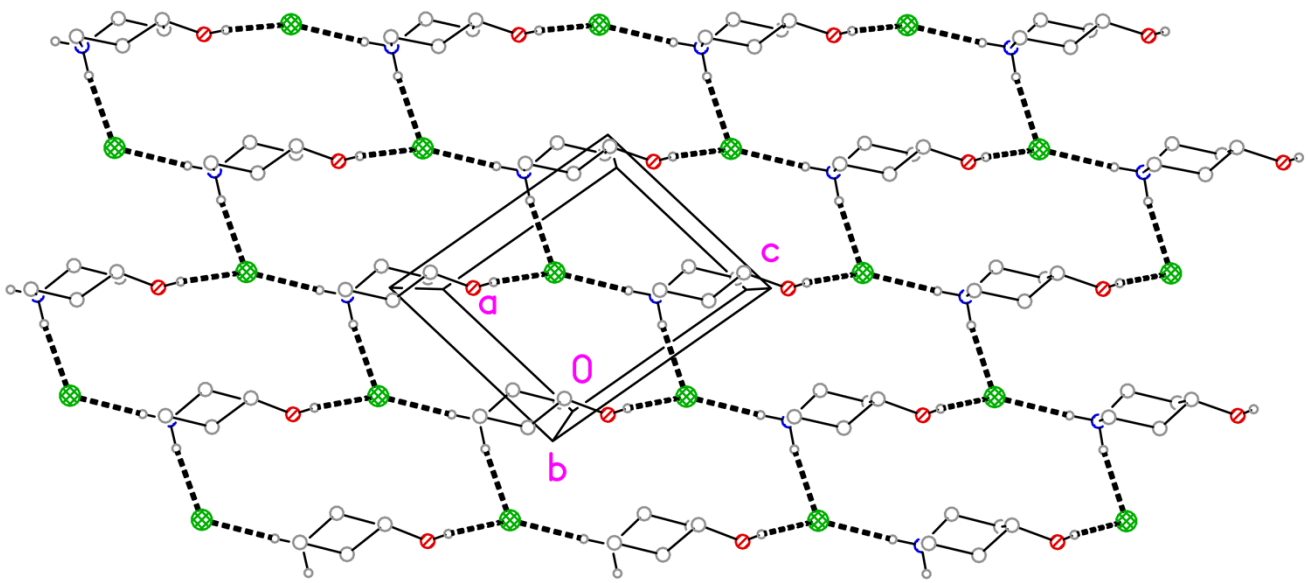

Figure S10. Packing diagram of compound **2** viewed parallel to the *b* axis in the region $y \approx 1/8$. Hydrogen bonds are indicated by thick dashed lines.

Compound 3

Both OH groups act as H bond donors and acceptors to form infinite chains □O–H□O–H□O–H□ parallel to the *b* axis (Table S3, Fig. S11). The operator is the 2_1 screw axis in the same direction. The extended packing is a layer structure parallel to the *bc* plane. The layers consist of rings with the graph set $R_4^4(28)$.

Table S3. Classical hydrogen bonds [Å and °] for compound **3**.

D–H...A	d(D–H)	d(H□A)	d(D□A)	<(DHA)
O1–H01□O2#1	0.86(3)	1.91(3)	2.768(2)	170(3)
O2–H02□O1#2	0.85(3)	1.93(3)	2.783(2)	173(3)

Symmetry transformations used to generate equivalent atoms:
#1 –*x*+1, –*y*+1, *z*+1/2; #2 –*x*+1, –*y*+2, *z*–1/2.

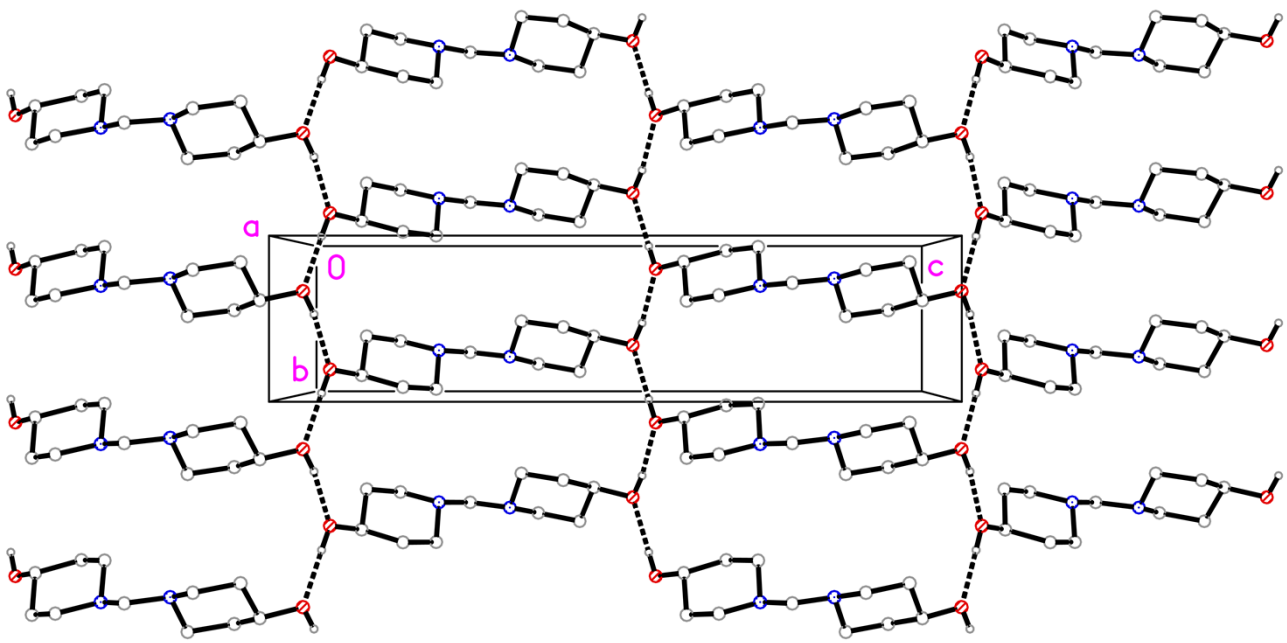

Figure S11. Packing diagram of compound **3** viewed parallel to the *a* axis. Hydrogen bonds are indicated by thick dashed lines.

Compound 4

The packing of compound **4** is extremely complicated. There are six independent residues and twelve independent classical H bonds (Tab. S4). Because the structure is only of peripheral interest to the main topic of polymorphism, we do not attempt to present packing diagrams.

Table S4. Classical hydrogen bonds [Å and °] for **4**.

D–H...A	d(D–H)	d(H□A)	d(D□A)	<(DHA)
N11–H01□O41#1	0.915(15)	1.791(16)	2.705(3)	176(3)
N11–H02□O51#1	0.935(15)	1.743(16)	2.667(3)	169(2)
N21–H03□O52	0.929(16)	1.865(18)	2.763(3)	162(3)
N21–H04□O42	0.942(15)	1.721(16)	2.652(3)	170(2)
N31–H05□O62	0.931(16)	1.783(16)	2.711(3)	175(3)
N31–H06□O61#2	0.936(17)	1.82(2)	2.716(3)	160(4)
O1–H07□O52#3	0.84	1.88	2.718(3)	174.0
O2–H08□O62#4	0.84	1.98	2.799(3)	166.3
O3–H09□O6#5	0.84	1.93	2.755(3)	167.2
O4–H010□O1	0.84	2.08	2.890(3)	161.8
O5–H011□O61#6	0.84	1.94	2.778(3)	173.7
O6–H012□O41#5	0.84	1.82	2.657(3)	175.6

Symmetry transformations used to generate equivalent atoms:

#1 *x*–1 ,*y* ,*z*; #2 –*x*+2, –*y*, –*z*+1; #3 –*x*, –*y*+1, –*z*+2; #4 –*x*+1, –*y*+1, –*z*+1; #5 –*x*+1, –*y*, –*z*+1; #6 *x*, *y*+1, *z*.