Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information:

Unusual Physical Behaviour and Polymorphic Phase Transitions in Crystalline Bicyclic Anhydrides

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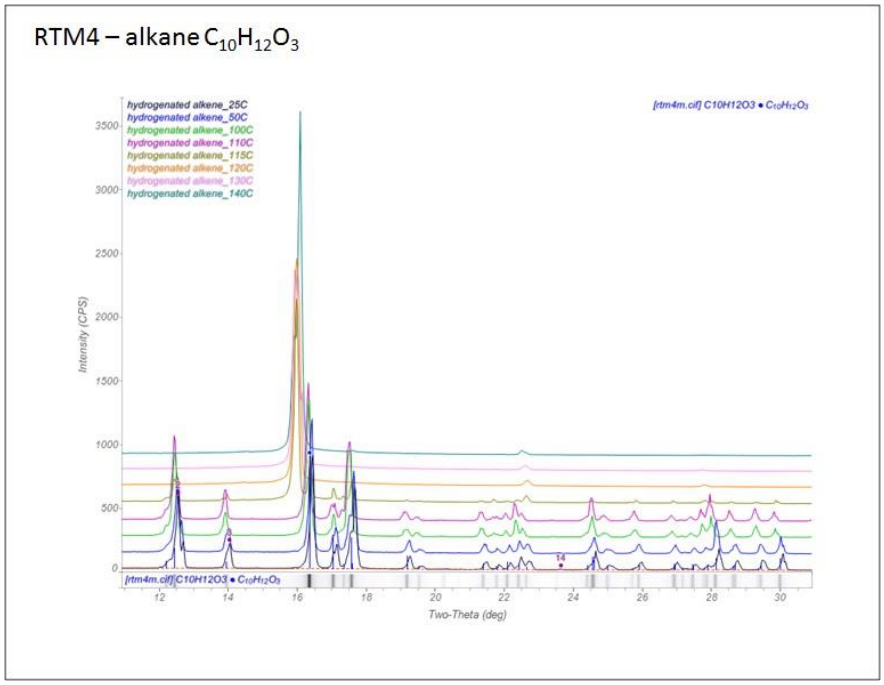
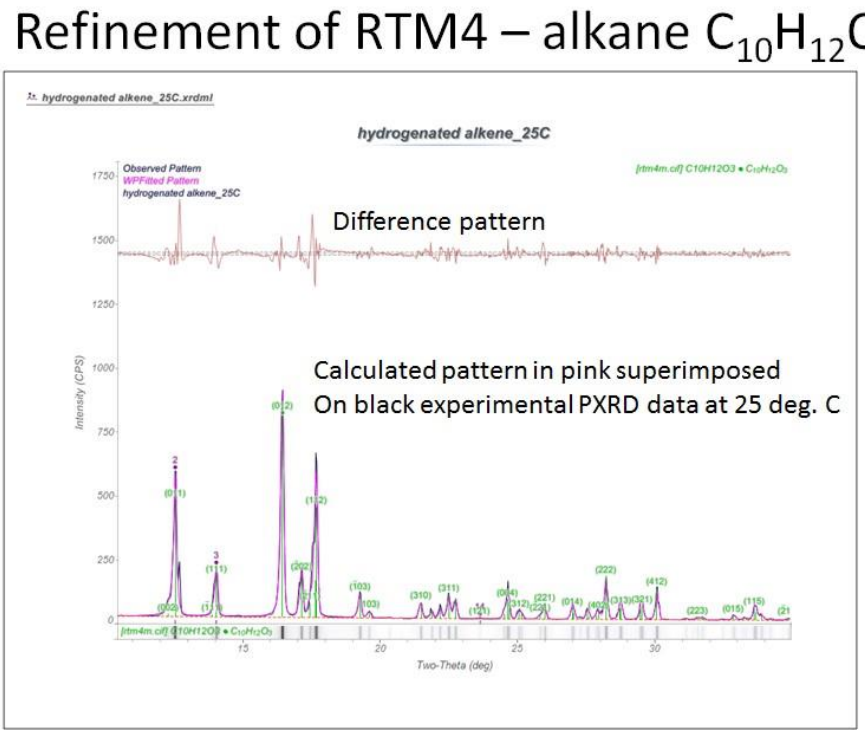


Overlay shows non-ambient alkane (RTM4) PXRD series as compared to the *.cif file which is mP21/n (14).

More or less a good match to ambient powder XRD data with some peak shift.

Figure S1

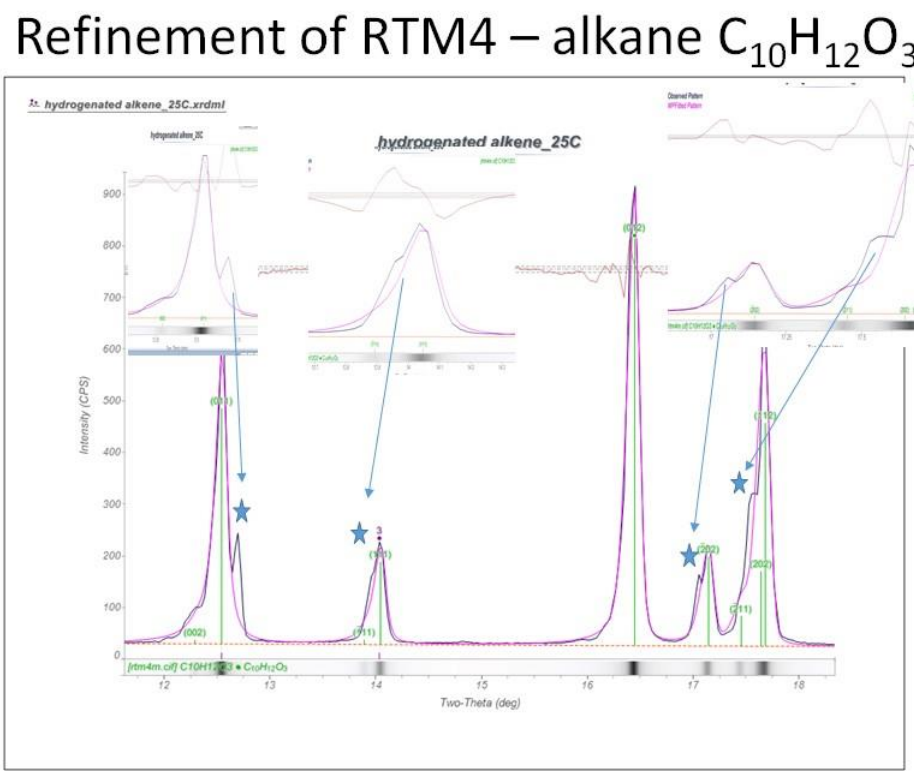


Refinement of PXRD data with rtm4.cif shows a reasonable fit but indicates that the material is not phase pure. This is likely the reason that PXRD could not index with this space group.

See next slide to see zoomed regions.

R=13.03% and E = 1.37%

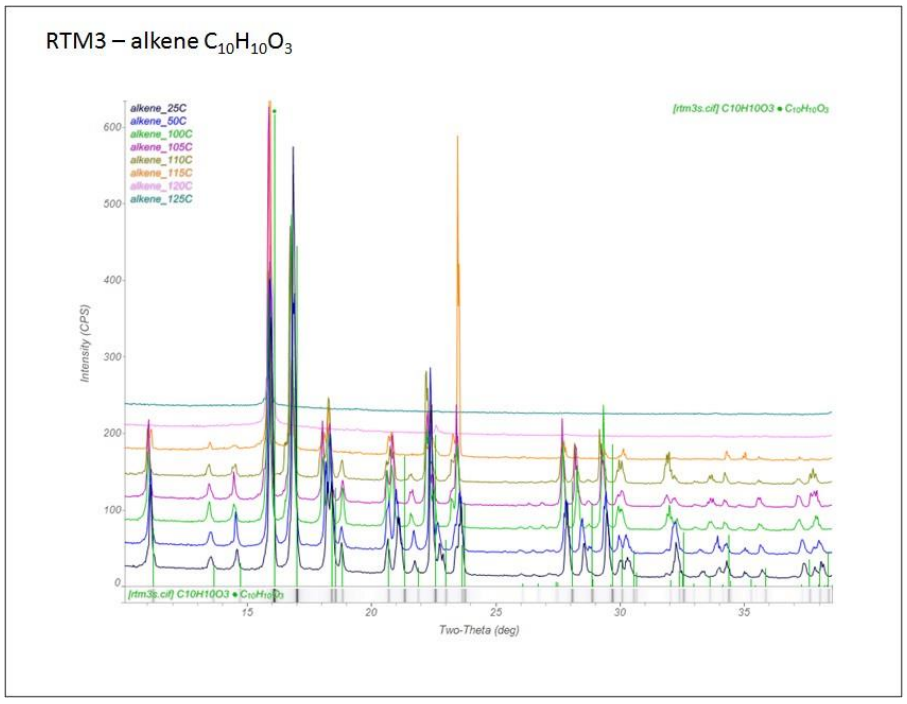
Figure S2



Note areas of large difference in the difference pattern marked by ★

These indicate the presence of a secondary phase(s).

Figure S3

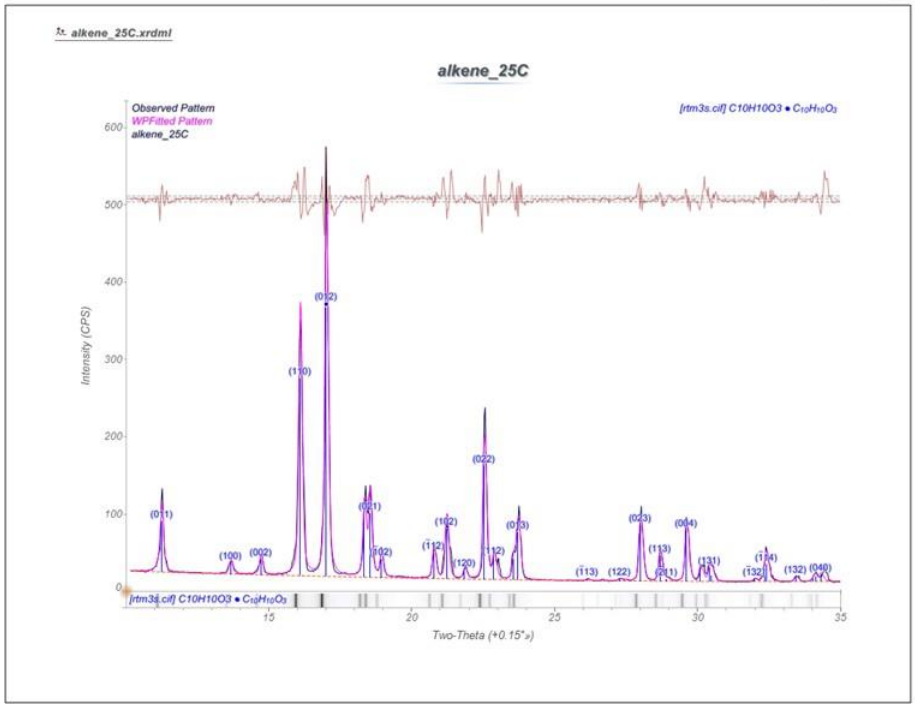


Overlay shows non-ambient alkene (RTM3) PXRD series as compared to the *.cif file which is mP21/c (14).

More or less a good match to ambient powder XRD data with some peak shift.

Figure S4

Refinement of RTM3 – alkene $C_{10}H_{10}O_3$



Refinement of PXRD data with rtm3.cif shows a good fit but also indicates that the material is not phase pure.

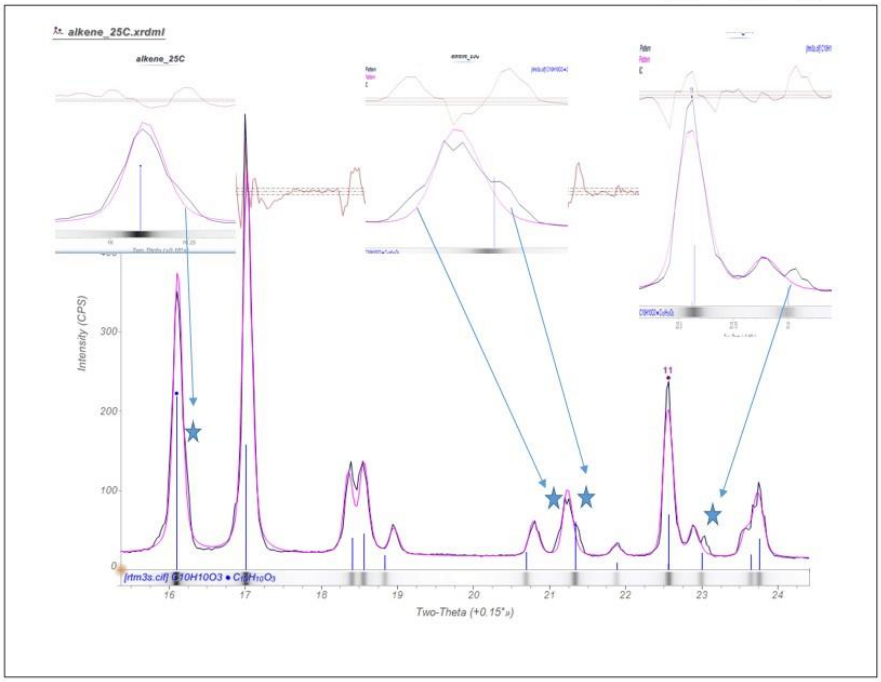
The peaks for the additional phase are located at higher 2-theta positions and are of lower overall intensity as compared to the additional peaks in RTM4 and thus would have lower weighting in the indexing process which is likely why this one was easily indexed as mP21/c (14).

See next slide to see zoomed regions.

R=11.25% and E = 1.73%

Figure S5

Refinement of RTM3 – alkene $C_{10}H_{10}O_3$



Note areas of largest difference in the difference pattern marked by ★

These indicate the presence of a secondary phase(s).

Figure S6

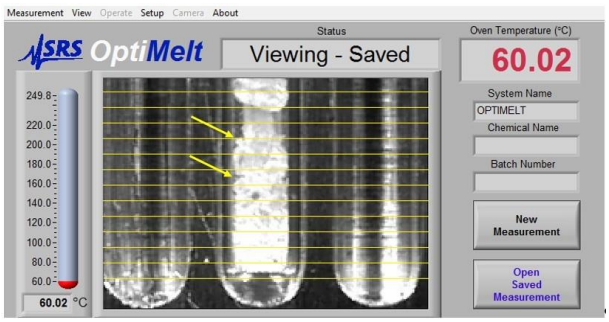


Figure S7. Screen shot on OptiMelt before phase transition temperature (RTM3); red arrows point to features with respect to stationary lines (in yellow)

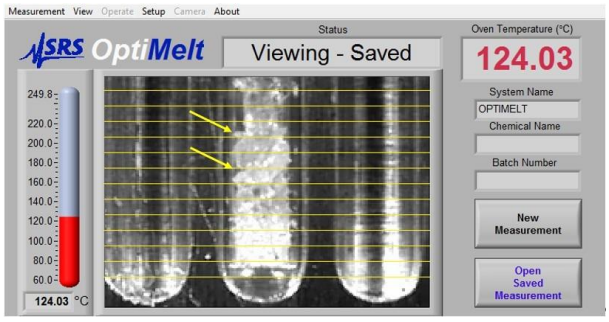


Figure S8. Screen shot on OptiMelt after phase transition temperature (RTM3); red arrows point to the same features which moved with respect to the stationary lines drawn on the image; this shift is due to crystal's expansion due to a phase transition (not due to thermal expansion)

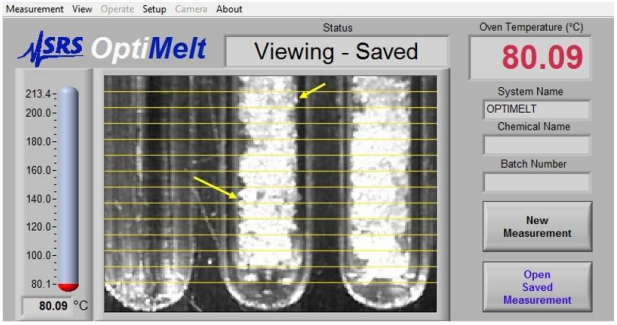


Figure S9. Screen shot on OptiMelt before phase transition temperature (RTM4); yellow arrows point to features with respect to stationary lines (in yellow).

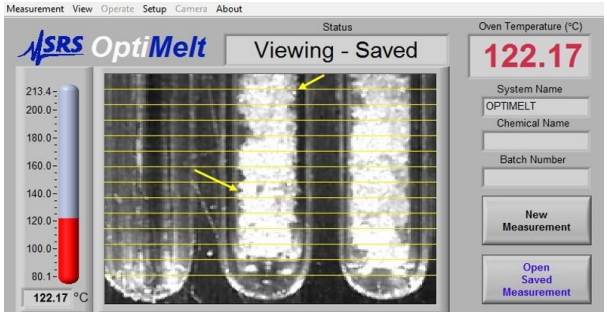


Figure S10. Screen shot on OptiMelt after phase transition temperature (RTM4); yellow arrows point to the same features which moved with respect to the stationary lines drawn on the image; this shift is due to crystal's expansion due to a phase transition (not due to thermal expansion).

Table S1. Single crystal X-ray diffraction summary for BCA1

Identification code	**BCA1**	
Empirical formula	C14 H18 O3	
Formula weight	234.28	
Temperature	298(2) K	
Wavelength	0.71073 Å, MoKα	
Crystal size	0.29 x 0.24 x 0.18 mm	
Crystal habit	colorless block	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.8700(18) Å	α= 90°
	b = 8.309(2) Å	β= 90°
	c = 22.230(6) Å	γ = 90°
Volume	1268.9(6) $Å^3$	
Z	4	
Density (calculated)	1.226 g/cm^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	504	
Theta range for data collection	1.83 to 28.36°	
Index ranges	$-8 \le h \le 6$, $-9 \le k \le 11$, $-29 \le l \le 29$	
Total number of reflections	8269	
Θ_{max}	28.36° (0.90 Å resolution),	
Unique, >2σ (I) reflections	3065, 2479	
Completeness	96.3%	
R_{int}, R_{sig},	0.0206, 0.0251	
$R_1[F^2 > 2\sigma(F^2)]$, ${}_wR_2(F^2)$, S	0.0453, 0.1179, 1.065	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.154, -0.230	

Table S2. Single crystal X-ray diffraction summary for BCA2

Identification code	**BCA2**	
Empirical formula	C14 H20 O3	
Formula weight	236.30	
Temperature	298(2) K	
Wavelength	0.71073 Å, MoKα	
Crystal size	0.19 x 0.18 x 0.15 mm	
Crystal habit	colorless cubical	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.9562(18) Å	α= 90°
	b = 8.559(2) Å	β= 90°
	c = 21.752(6) Å	γ = 90°
Volume	1295.0(6) $Å^3$	
Z	4	
Density (calculated)	1.212 g/cm^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	512	
Theta range for data collection	1.87 to 28.31°	
Index ranges	$-9 \le h \le 9$, $-11 \le k \le 10$, $-28 \le l \le 28$	
Total number of reflections	7213	
Θ_{max}	28.31° (0.90 Å resolution),	
Unique, >2σ (I) reflections	2952, 2074	
Completeness	94.4%	
R_{int}, R_{sig},	0.0331, 0.0453	
$R_1[F^2 > 2\sigma(F^2)]$, $_wR_2(F^2)$, S	0.0496, 0.1413, 1.012	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.134, -0.182	

Table S3. Single crystal X-ray diffraction summary for RTM3

Identification code	**rtm3**	
Empirical formula	C10 H10 O3	
Formula weight	178.18	
Temperature	203(2) K	
Wavelength	0.71073 Å, MoKα	
Crystal size	0.22 x 0.16 x 0.13 mm	
Crystal habit	colorless block	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 6.5300(15) Å	α= 90°
	b = 10.411(2) Å	β= 97.062(4)°
	c = 12.121(3) Å	γ = 90°
Volume	817.7(3) $Å^3$	
Z	4	
Density (calculated)	1.447 g/cm^3	
Absorption coefficient	0.107 mm^{-1}	
F(000)	376	
Theta range for data collection	2.59 to 28.26°	
Index ranges	$-8 \le h \le 8$, $-13 \le k \le 6$, $-13 \le l \le 16$	
Total number of reflections	3852	
Θ_{max}	28.26° (0.90 Å resolution),	
Unique, >2σ (I) reflections	1998, 1710	
Completeness	98.4%	
R_{int}, R_{sig},	0.0151, 0.0248	
$R_1[F^2 > 2\sigma(F^2)]$, $_wR_2(F^2)$, S	0.0466, 0.1233, 1.026	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.277, -0.219	

Table S4. Single crystal X-ray diffraction summary for RTM4

Identification code	**rtm4**	
Empirical formula	C10 H12 O3	
Formula weight	180.20	
Temperature	203(2) K	
Wavelength	0.71073 Å, MoKα	
Crystal size	0.20 x 0.18 x 0.14 mm	
Crystal habit	colorless pyramid	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.472(3) Å,	α= 90°
	b = 8.1530(17) Å,	β= 91.730(4)°
	c = 14.494(3) Å,	γ = 90°
Volume	1709.4(6) $Å^3$	
Z	8	
Density (calculated)	1.400 g/cm^3	
Absorption coefficient	0.103 mm^{-1}	
F(000)	768	
Theta range for data collection	2.02 to 28.37°	
Index ranges	$-18 \le h \le 19$, $-9 \le k \le 10$, $-17 \le l \le 19$	
Total number of reflections	10819	
Θ_{max}	28.37° (0.90 Å resolution),	
Unique, >2σ (I) reflections	4107, 2984	
Completeness	96.2%	
R_{int}, R_{sig},	0.0216, 0.0263	
$R[F^2 > 2\sigma(F^2)]$, $wR_2(F^2)$, S	0.0506, 0.1359, 1.026	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.159, -0.271	

Table S5. Energies used in the calculation of sublimation enthalpies. Corrected energy per molecule is calculated as (DFT Energy + ZPE + Enthalpy)/Z.

Structure	DFT Energy (eV)	ZPE (eV)	Enthalpy @ 298K (eV)	Corrected Energy Per Molecule (eV)
BCA1 (C=C Bond)				
Gas (Z = 1)	-3749.265141184	7.79309308	0.385313	-3741.086735104
Crystal (Z = 4)	-15002.90641337	33.66921766	0.993964	-3742.060807928
BCA2 (C-C Bond)				
Gas (Z = 1)	-3782.275026036	8.449551438	0.382722	-3773.442752598
Crystal (Z = 4)	-15134.78212106	36.2626037	1.052156	-3774.36684034
RTM3S (C=C Bond)				
Gas (Z =1)	-3000.382740346	4.89184106	0.28000	-2995.21089929
Crystal (Z = 4)	-12006.72667432	19.9946748	0.82440	-2996.47689988
RTM4M (C-C Bond)				
Gas (Z = 1)	-3033.639157777	5.52883294	0.26700	-3027.843324837
Crystal (Z = 8)	-24279.71572825	45.8653701	1.83300	-3029.002169769

Figure S11. 3D representation of RTM3, RTM4, BCA1, and BCA2 molecular units.

RTM3	RTM4	BCA1	BCA2