Supplementary Information:

Controlling the distance between hydrogen-bonded chloro-*s*-triazine tapes: crystal engineering using *N*-alkyl chains and the influence of temperature

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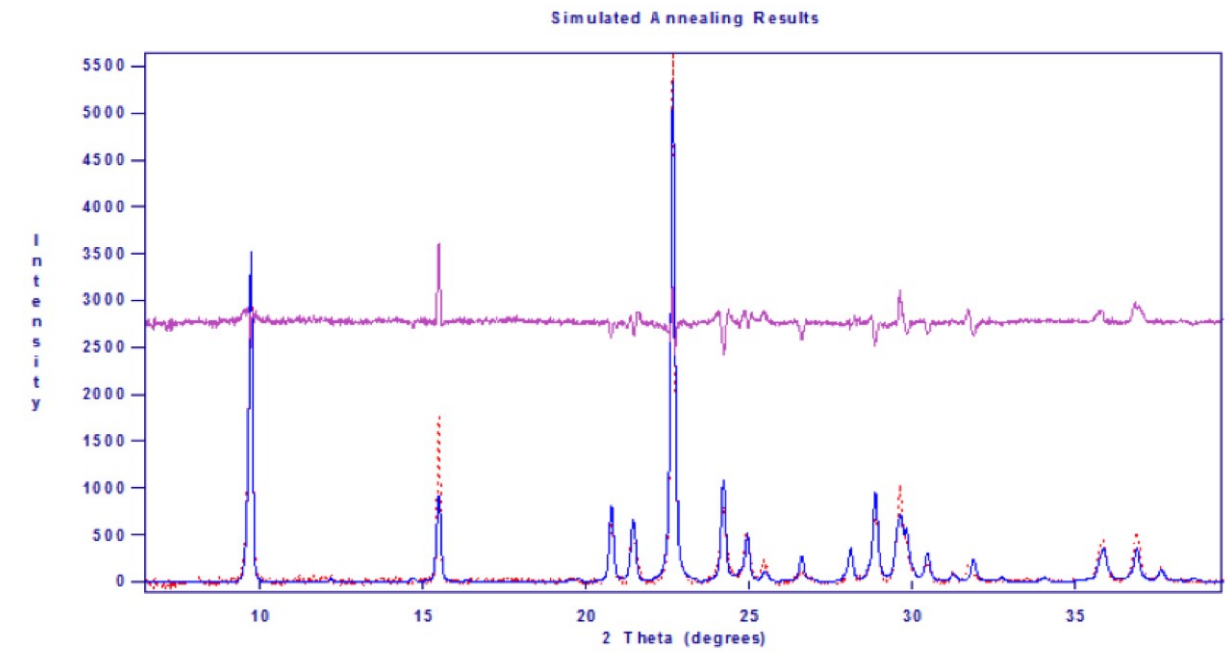
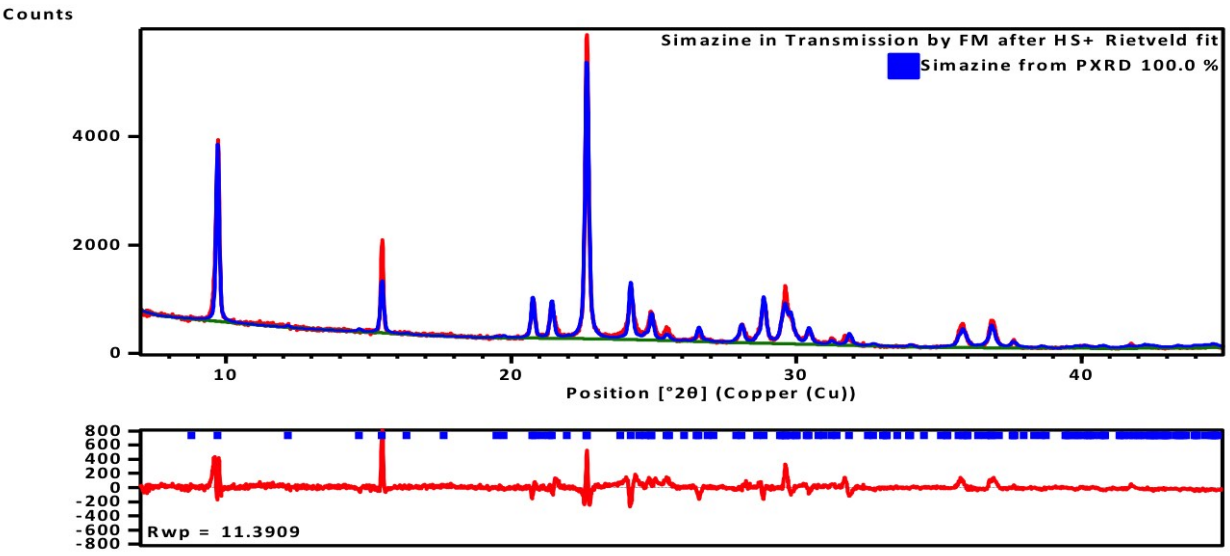
Table S1: Details of single-crystal analysis of mono-*N*-butyl **3a** and mono-*N*-pentyl **3b**.

	3a (100 K)	**3b** (100 K)
Chemical formula	$C_7H_{10}Cl_2N_4$	$C_8H_{12}Cl_2N_4$
M_r	221.09	235.12
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$
CCDC deposition number	1552799	1552800
Temperature (K)	100	100
a	5.012(1)	25.548(5)
b	11.794(2)	5.000(1)
c (Å)	17.086(3)	9.343(4)
α	86.52(3)	
β	84.11(3)	115.30(3)
γ (°)	82.67(3)	
V (Å^3)	995.3(4)	2233.8(9)

Z	4	8
Radiation type	0.71073 Å	0.71073 Å
μ (mm^{-1})	0.61	0.55
Crystal size (mm)	0.02 × 0.02 × 0.01	0.02 × 0.02 × 0.01
Data collection		
Diffractometer	Australian Synchrotron	Australian Synchrotron
Absorption correction	-	-
T_{min}, T_{max}	-	-
No. of measured, independent and observed [$I > 2s(I)$] reflections	12269, 3181, 2979	12722, 1841, 1673
R_{int}	0.018	0.022
$(\sin q/l)_{max}$ ($Å^{-1}$)	0.595	0.594
Refinement		
$R[F^2 > 2s(F^2)]$	0.030	0.038,
$wR(F^2)$	0.077	0.096
S	1.08	1.12
No. of reflections	3181	1841
No. of parameters	237	128
No. of restraints	0	0
H-atom treatment	Constrained	Constrained
$D\tilde{n}_{max}$, $D\tilde{n}_{min}$ (e $Å^{-3}$)	0.24, -0.27	0.25, -0.40



(a)



(b)

Figure S1: Experimental and calculated powder diffraction patterns for **1a** (298 K) obtained from (a) structure solution using simulated annealing in DASH and (b) Rietveld refinement of peak profiles using HighScore plus**.**

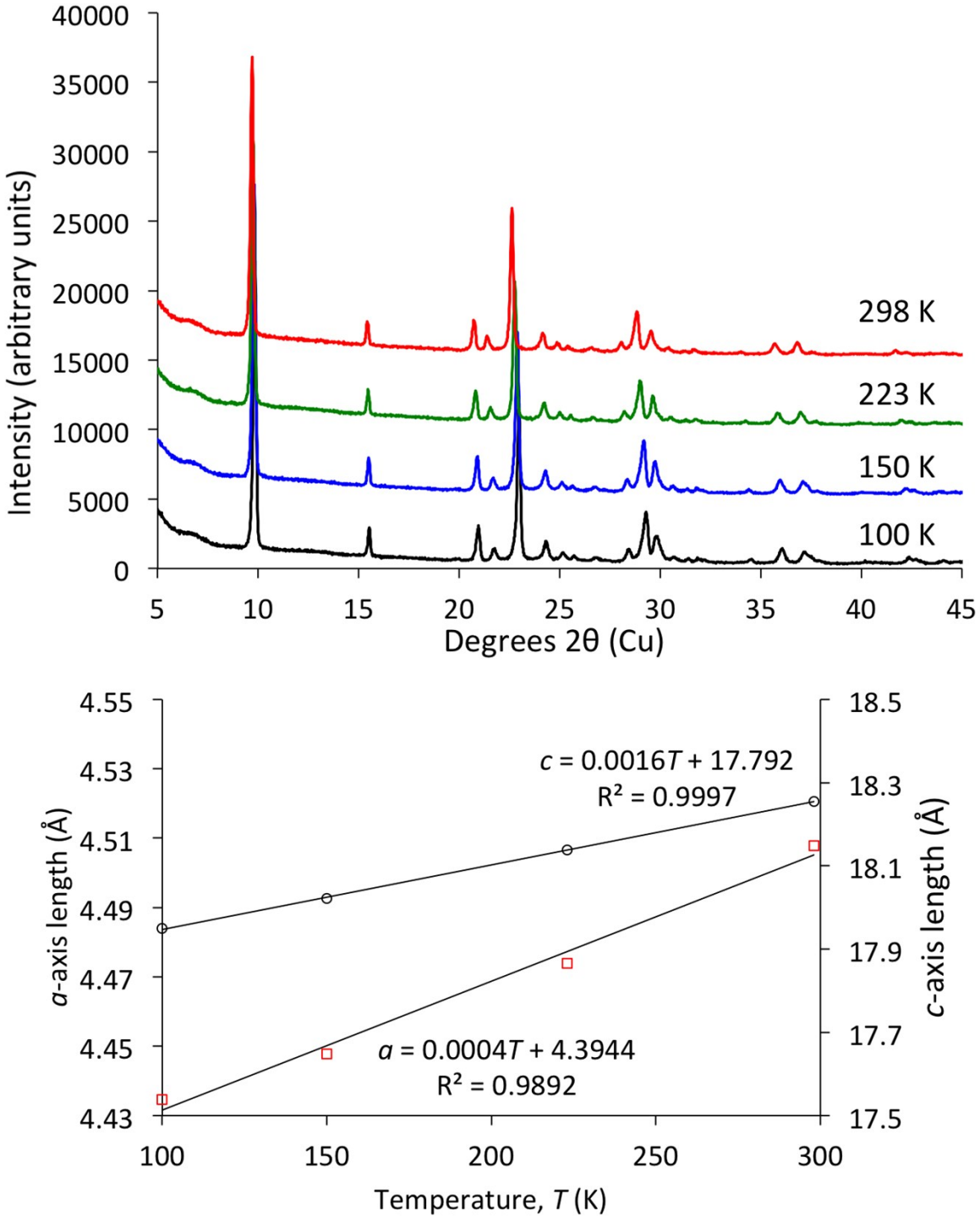


Figure S2: Variation of powder diffraction pattern of **1a** showing decrease in peak position with increasing temperature from 100 K to 298 K (top). The cell axes show small, linear changes with temperature, with the *a*–axis and *c*-axis increasing by 1.7% while the *b*-axis (not shown) increases by 0.6%.

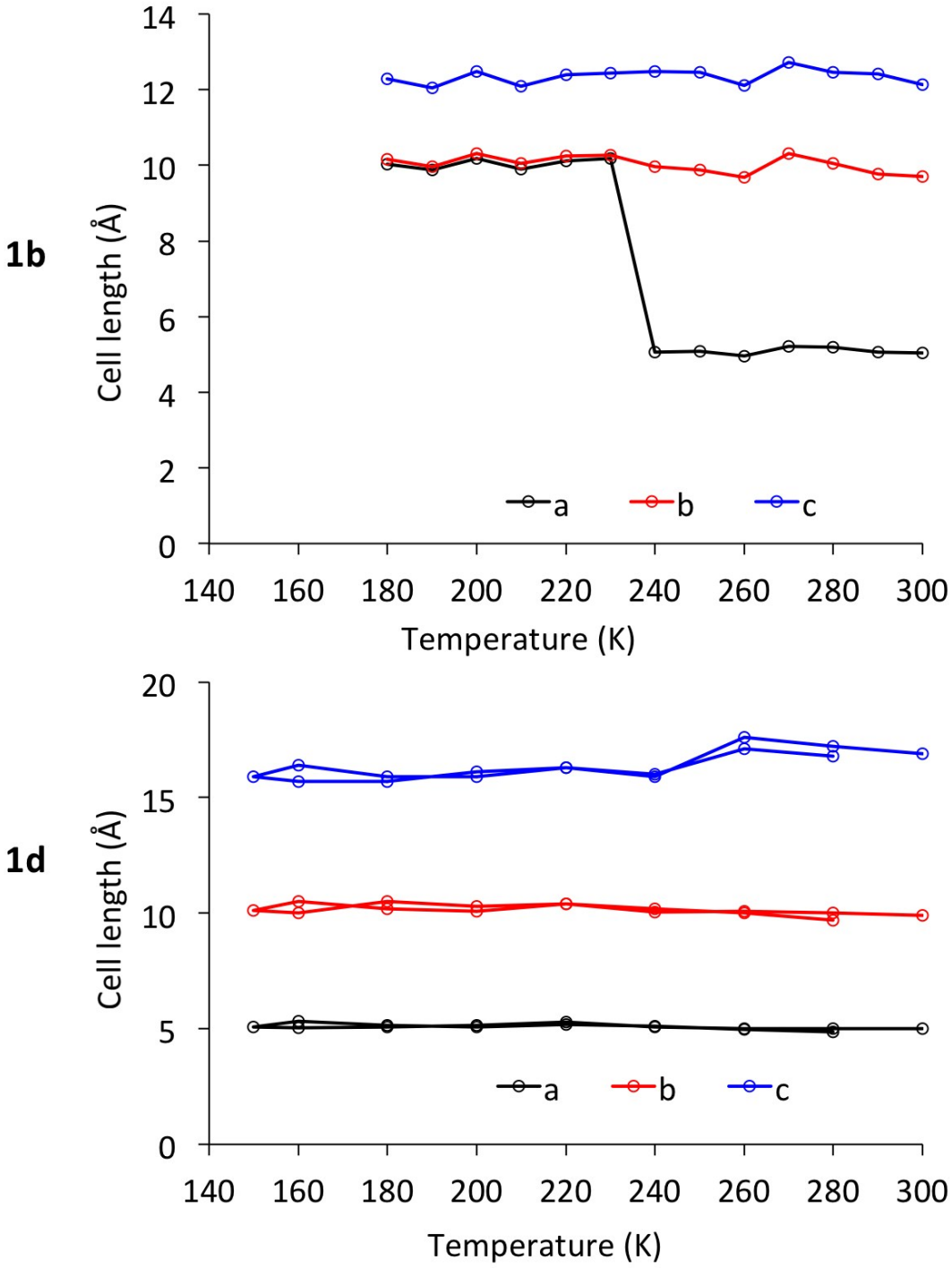


Figure S3: Structural transitions occurring with increasing temperature in the odd-carbon number derivatives, bis-*N*-propyl **1b** and bis-*N*-pentyl **1d**. Major transition in **1b** occurs between 230-240 K, with a possible second transition between 260-270K. The major transition in **1d** occurs between 240-260 K.

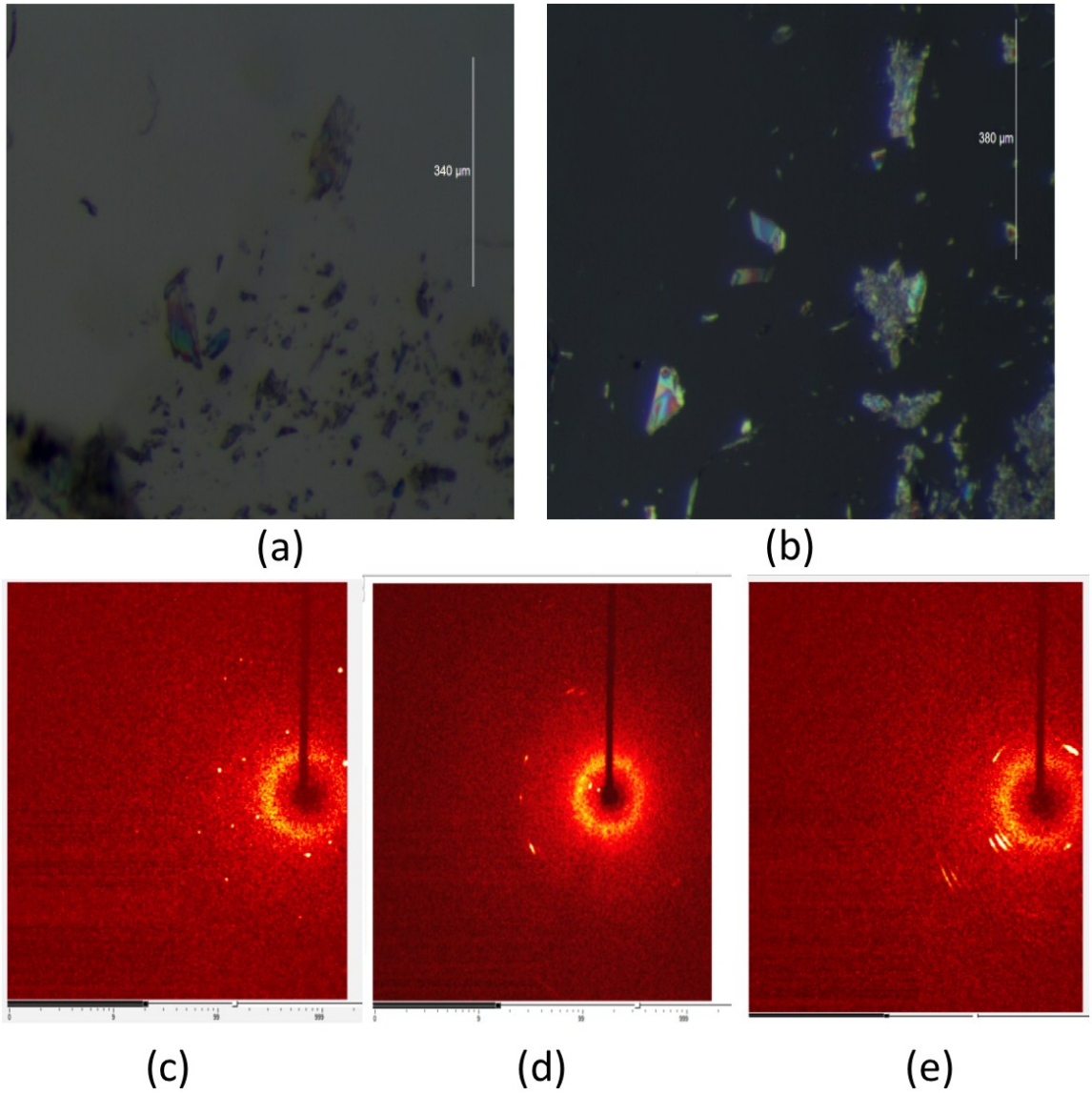
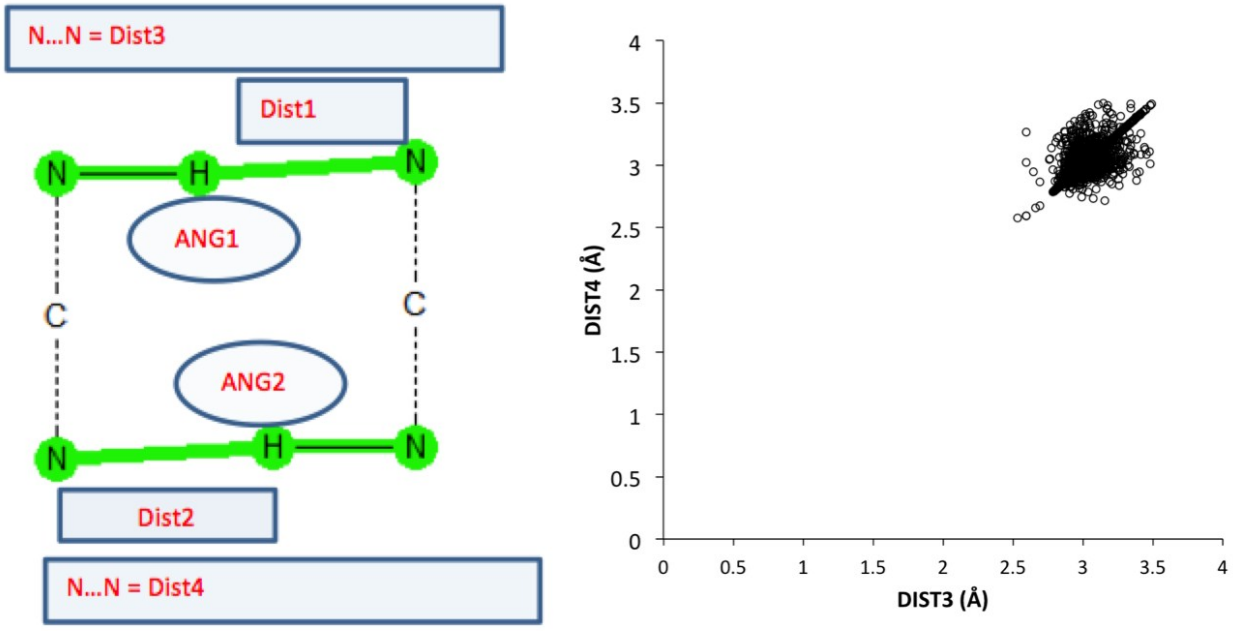


Figure S4: Diffraction behaviour of bis-*N*-pentyl **1d** and bis-*N*-hexyl **1e**. Micrographs of the crystals of (a) bis-*N*-pentyl **1d** and (b) bis-*N*-hexyl **1e** show similar thin plates, however, their diffraction behavior was significantly different. The bis-*N*-pentyl **1d** derivative at 150K showed sharp diffraction spots that extended to a reasonably high resolution (c) and subsequent structure solution revealed no disorder in the alkyl chains. The same crystal at room temperature (298 K) had weak diffraction and streaky spots in most regions (d) that we associated with the disordered alkyl chains. At 150 K the bis-*N*-hexyl **1e** showed very streaky diffraction spots (e) that we associate with highly disordered alkyl chains in its crystal lattice.



(a) (b)

Figure S5: (a) CCDC Search criteria for the self-complementary NH...N interaction, and (b) spread of both N...N distance values around the mean of 3.03 Å.

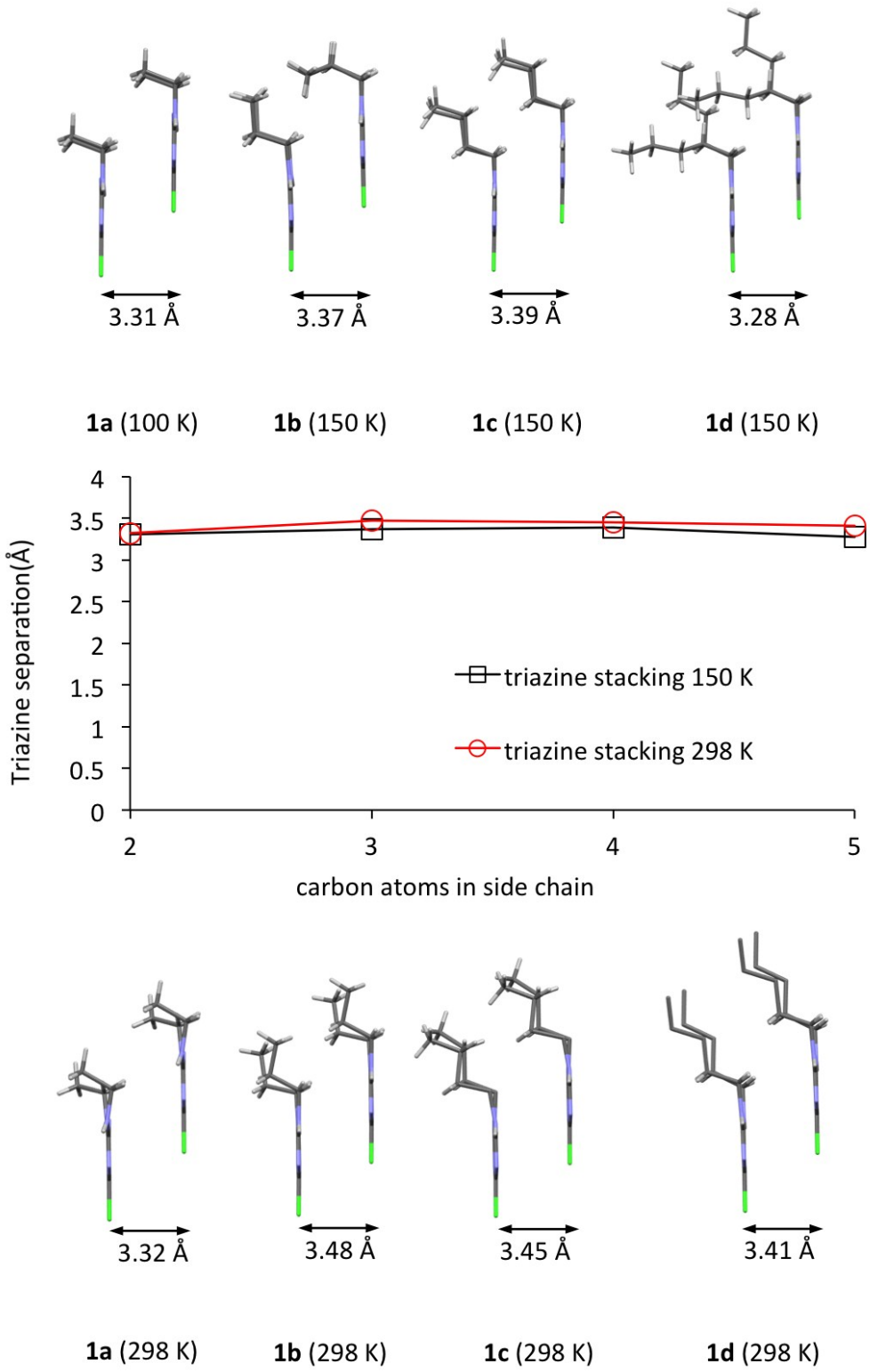


Figure S6: Stacking distance between the triazine rings is relatively unaffected by the alkyl chain length and temperature.