

Supporting Information

Shape segregation in molecular organisation: a combined X-ray scattering and molecular dynamics study of smectic liquid crystals

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Determination of experimental translational order parameters

X-ray scattering intensities plotted against 2θ are shown for 11OCB and *t*-Bu-11OCB in Figure S1 (a) and Figure S2 (a), respectively. A linear offset defined by the intensity at the 2θ limits of each of the datasets was applied before determining the integrated intensity. Data were fitted to Equation (4) in the main text, and plots of integrated intensity against temperature are shown in Figure S1 (b) and Figure S2 (b), along with the fits and curves corresponding to the 95% confidence intervals for I_0 . All of the fitted values and their associated 95% confidence intervals are listed in Table S1. The values of I_0 are within error of one another for the two compounds, consistent with their very similar molecular structures, and the values of T_c , the superheating limit of the SmA phase, are on the order of the experimental SmA – Iso transition temperatures. The value of β for 11OCB is almost twice that for *t*-Bu-11OCB, arising from the greater temperature dependence of the integrated intensity for 11OCB than *t*-Bu-11OCB.

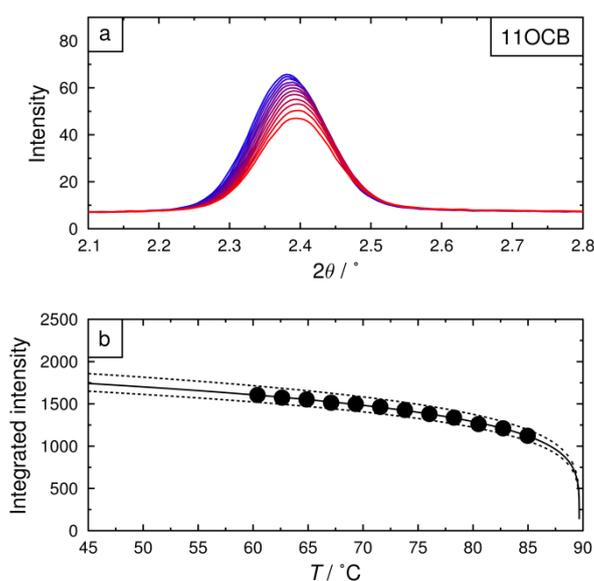


Figure S1 Plots of (a) scattered intensity against 2θ and (b) integrated intensity against temperature, along with a curve showing the fit to Equation (4) (solid line) and curves arising from the 95% confidence intervals for I_0 (dashed lines) for 11OCB.

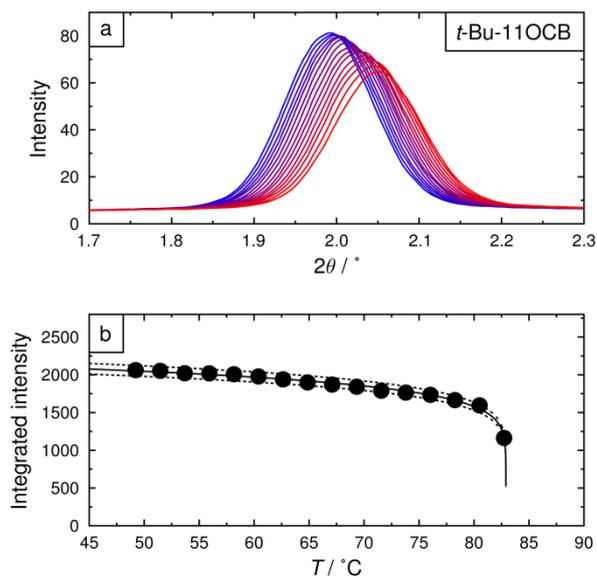


Figure S2 Plots of (a) scattered intensity against 2θ and (b) integrated intensity against temperature, along with a curve showing the fit to Equation (4) (solid line) and curves arising from the 95% confidence intervals for I_0 (dashed lines) for *t*-Bu-11OCB.

Table S1 Fitted parameters from Equation S1 for 11OCB and *t*-Bu-11OCB. Ranges given in brackets correspond to the 95 % confidence intervals.

	I_0	$T_C / ^\circ\text{C}$	β
11OCB	2625 (2488 – 2801)	89.7 (88.4 – 91.4)	0.0979 (0.0869 – 0.1121)
<i>t</i> -Bu-11OCB	2635 (2549 – 2728)	82.9 (82.8 – 83.0)	0.0531 (0.0477 – 0.0588)

Analysis of the smectic character of the simulated phases

The smectic characters of the simulated phases were analysed by determining the angle, $\angle \mathbf{n}\mathbf{k}$, between the director, \mathbf{n} , and the layer normal, \mathbf{k} , for each frame. Histograms of the normalised orientational distribution functions for this angle, $f(\angle \mathbf{n}\mathbf{k})$, were obtained *via* the populations in the simulations, corresponding to $f(\angle \mathbf{n}\mathbf{k})\sin(\angle \mathbf{n}\mathbf{k})$, and are shown in Figure S3. Both plots show maxima at $0^\circ < \angle \mathbf{n}\mathbf{k} < 2^\circ$, indicating that the director tends to align with the layer normal in both simulations. This analysis confirms the simulated phases to be of SmA character, as opposed to being SmC phases in which a maximum at significantly greater than 0° should be observed due to the molecules being tilted within the layers.

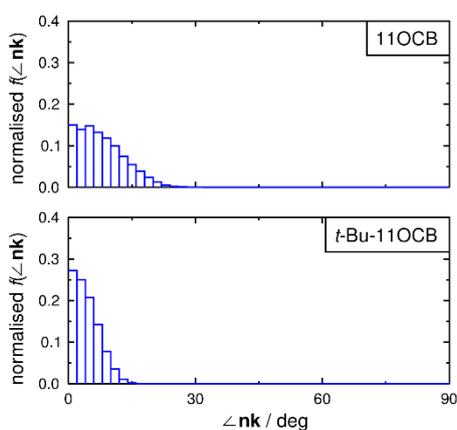


Figure S3 Histograms of normalised $f(\angle \mathbf{n}\mathbf{k})$ against $\angle \mathbf{n}\mathbf{k}$ over the respective analysis ranges (the last 1000 ns) of the simulations of 11OCB and *t*-Bu-11OCB, determined with 2° bin-widths.