1. Methods

1.1. General Techniques

4-((2,4-Dimethoxybenzoyl)oxy)benzoic acid was prepared as described previously; [1] EDC.HCl was purchased from Fluorochem, DMAP was purchased from SigmaAldrich, and solvents were purchased from Fisher Scientific. Reactions were monitored by thin layer chromatography (TLC) using an appropriate solvent system. Silica coated aluminium TLC plates used were purchased from Merck (Kieselgel 60 F-254) and visualised using UV light (254 nm). Column chromatography was performed using flash grade silica from Fluorochem (40 - 63μm particle size).

1.2. Nuclear Magnetic Resonance

NMR spectra were recorded on a JEOL ECS spectrometer operating at 400 MHz (^{1}H) or 100.5 MHz (^{13}C{^{1}H}) as solutions in deuterated chloroform. Spectra were referenced to the residual protic solvent for ^{1}H (7.26 ppm), ^{13}C{^{1}H} to the resonance of CDCl$_3$ (77.16 ppm).

1.3. Mass Spectrometry

Mass spectra were recorded on a Bruker compact time of flight mass spectrometer with both ESI and APCI sources, and we extend our gratitude to Mr. Karl Heaton of the University of York for obtaining MS data.

1.4. Polarised Optical Microscopy

Polarised optical microscopy was performed on a Zeiss Axioskop 40Pol microscope using a Mettler FP82HT hotstage controlled by a Mettler FP90 central processor. Photomicrographs were captured *via* either an InfinityX-21 MP digital camera (1 MP) or a Sony NEX 5R mirrorless digital camera (16 MP) mounted atop the microscope. Analysis of image profiles was performed in Matlab.

1.5. Differential Scanning Calorimetry.

Differential scanning calorimetry was performed on a Mettler DSC822^e fitted with an autosampler operating with Mettler Star^e software and calibrated before use against an indium standard (onset = 156.55 ± 0.2 °C, ΔH = 28.45 ± 0.40 Jg^{-1}) under an atmosphere of dry nitrogen.

1.6. X-ray scattering

Small angle X-ray diffraction was performed using a Bruker D8 Discover equipped with a temperature controlled, bored graphite rod furnace, custom built at the University of York. The radiation used was copper Kα from a 1 μS microfocus source. Diffraction patterns were recorded on a 2048x2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample, allowing simultaneous collection of small angle and wide angle scattering data. Samples were filled into 1mm capillary tubes and aligned with a pair of 1T magnets. Diffraction patterns were collected as a function of temperature. Background subtraction and data processing was performed in Matlab.

1.7. Computational Chemistry

Quantum chemical calculations were performed using the Gaussian 09 revision e01 suite of programmes. [2] Output files were aligned and visualised using VMD. [3]

2. Chemical Characterisation
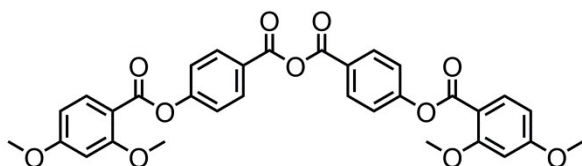
1: 4-((2,4-dimethoxybenzoyl)oxy)benzoic anhydride

A suspension of 4-((2,4-dimethoxybenzoyl)oxy)benzoic acid (302 mg, 1 mmol), [1] EDC.HCl (382 mg, 1 mmol), and DMAP (1 mg) in anhydrous THF (5 ml) was vigorously stirred for 24 h. The solvent was then removed *in vacuo*. The crude material was passed through a plug of SiO_2, eluting with 3:1 EtOAc/hexanes. The chromatographed material was recrystalised from toluene, giving the title compound as a colourless crystalline solid.

Yield: 240 mg (82 %)

Rf: 0.53 (DCM)

[1] H NMR: 3.89 (6H, s, ArO-CH₃), 3.93 (6H, s, ArO-CH₃), 6.53 (2H, d, *J* = 2.3 Hz, ArH), 6.57 (2H, dd, *J* = 2.3 Hz, *J* = 8.8 Hz, ArH), 7.37 (4H, ddd, *J* = 2.3 Hz, *J* = 3.3 Hz, *J* = 9.3 Hz, ArH), 8.07 (2H, d, *J* = 8.8 Hz, ArH), 8.28 (4H, ddd, *J* = 2.3 Hz, *J* = 3.3 Hz, *J* = 9.3 Hz, ArH)

$^{13}C\{^1H\}$ NMR: 55.78, 56.19, 99.12, 105.30, 110.53, 121.90, 127.99, 130.59, 134.01, 154.16, 161.66, 162.41, 164.08, 166.61

MS (APCI):   587.1577 (calcd. for $C_{32}H_{26}O_{11}$: 587.1548, M + H)

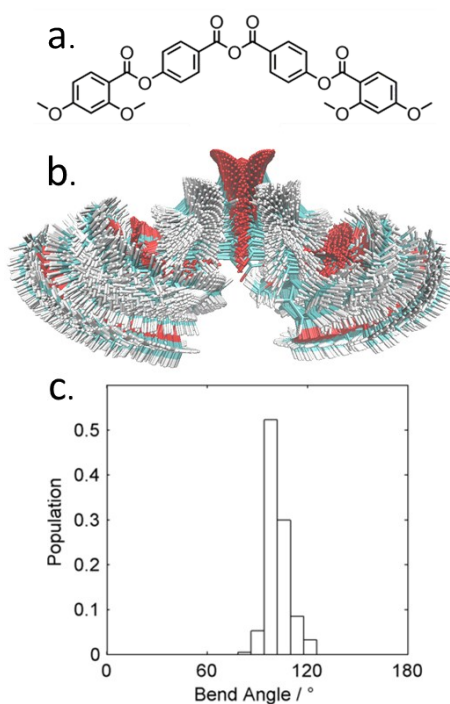### 3.   Conformational Analysis of Compound 1

Figure SI1:   (a) Molecular structure of compound **1**; (b) overlaid conformers of compound **1** calculated as described in the text at the wB97XD/6-31G(d) level of DFT; (c) probability distribution of bend angles of compound **1**.

We considered that compound **1** may exhibit some unexpected shape due to the presence of a central carboxylic acid anhydride, and so we performed fully relaxed scans on compound **1** (at the wB97XD/6-31G(d) level of DFT), allowing the two C(O)-O bonds of the carboxylic acid anhydride to undergo rotation (15 ° step size) while also allowing carboxylate esters to undergo twofold rotation about the C_{Ar}-C(O) and C_{Ar}-O bonds to give a library of conformers (Figure SI1). Assuming a Boltzmann population at 298 K, we calculate the probability weighted average bend angle to be centred on 100 ° with a FWHM of 12 °, we consider this typical for a 'semi-rigid' bent-core material.

4. Periodicity Measurements

As discussed in the manuscript we measured the splay-periodicity for binary mixtures of 34 wt% of **1** and 66 wt% of **3** using 5 micron thick cells with rubbed polyimide alignment surfaces to give planar alignment in the higher temperature nematic phase. Using the methodology described in the manuscript we measured the splay-periodicity for this same mixture confined in cells with a spacing of 3 μm and 9 μm (Figure SI2). We find mean and median periodicities of 9.4 μm and 9.0 μm respectively in the 3 μm cell, and mean and median periodicities of 9.8 μm and 9.0 μm respectively in the 9 μm cell. The values are not significantly different from those obtained when the sample is confined in a 5 μm cell, indicating that the splay modulation period is not perturbed by variations in cell gap.
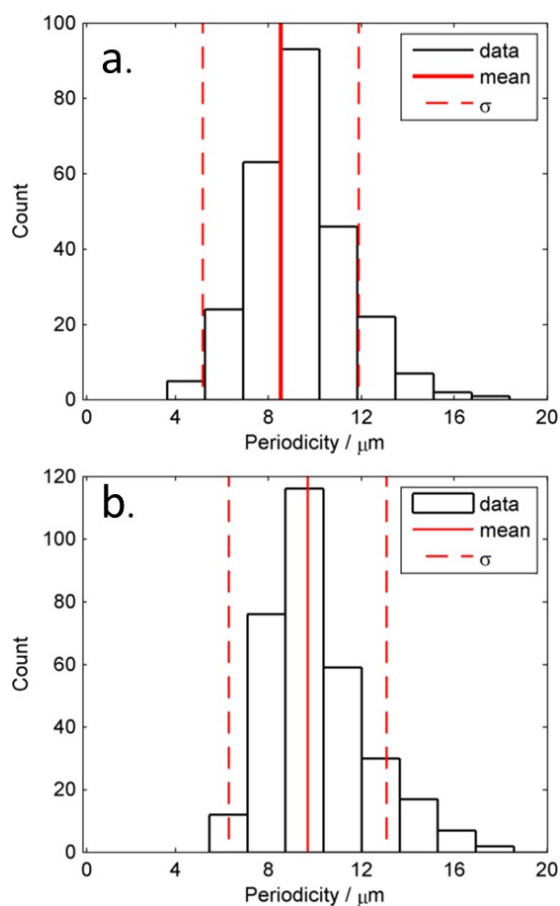

Figure SI2:   Histogram of measured optical periodicity from image profiles obtained for filled with binary mixtures of **1** and **3** (34 wt% **1**) filled into cells with a spacing of 3 μm (a) and 9 μm (b) between the two substrates.

5. References

1. R. J. Mandle, S. J. Cowling and J. W. Goodby, *Chem-Eur J*, 2017, **23**, 14554-14562.
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3. W. Humphrey, A. Dalke and K. Schulten, *J Mol Graph*, 1996, **14**, 33-38, 27-38.