# Supplementary Information for

# Intercalated Soft-Crystalline Mesophase Exhibited by an Unsymmetrical Twist-Bend Nematogen

Richard J. Mandle\* and John W. Goodby

Department of Chemistry, the University of York, Heslington, York, YO10 5DD.

# Contents

- **1.1.** General Methods
- **1.2.** Synthetic Details and Chemical Characterisation
- **1.3.** Tabulated Differential Scanning Calorimetry Data
- **1.4.** Supplemental DSC data
- **1.5.** Supplemental NMR spectra
- **1.6.** Supplemental HPLC Chromatographs
- **1.7.** Supplemental Small Angle X-Ray Scattering Data
- **1.8.** Gaussian Output Archive
- **1.9.** References

## 1.1. General Methods.

1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDAC) was purchased from Carbosynth UK, *N*,*N*-dimethylaminopyridine (DMAP) was purchased from Sigma Aldrich. Solvents were purchased from Fisher Scientific UK and were dried *via* passage over activated alumina prior to use. Nonane-1,9-diylbis(4,1-phenylene) bis(4-cyanobenzoate) (*i1*) was prepared as described previously. [1] Reactions were monitored by thin layer chromatography (TLC) with DCM as the eluent. Silica coated aluminium TLC plates used were purchased from Merck (Kieselgel 60 F-254) and visualised using either UV light (254 nm and 365 nm), or by oxidation with either iodine or aqueous potassium permanganate solution. Yields refer to chromatographically (HPLC) and spectroscopically (<sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR) homogenous material.

NMR spectra were recorded on a JEOL ECS spectrometer operating at 400 MHz (<sup>1</sup>H) or 100.5 MHz (<sup>13</sup>C{<sup>1</sup>H}) as solutions in CDCl<sub>3</sub>, unless stated otherwise. Mass spectra were recorded on a Bruker micrOTOF MS-Agilent series 1200LC spectrometer. High-performance liquid chromatography was performed on a Shimadzu Prominence modular HPLC system comprising a LC-20A solvent pump, a DGU-20A<sub>5</sub> degasser, a SIL-20A autosampler, a CBM-20A communication bus, a CTO-20A column oven, and a SPO-20A dual wavelength UV-vis detector. Purity was assayed using two different stationary phases: reverse-phase chromatography was performed using an Alltech C18 bonded silica column with a 5  $\mu$ m pore size, an internal diameter of 4.6 mm and a length of 250 mm whilst an Ascentis SI silica column with a 5  $\mu$ m pore size, an internal diameter of 4.6 mm and a length of 250 mm was used for 'normal' phase chromatography. Assays denoted 'HPLC' are normal phase; those denoted 'RP-HPLC' are reverse-phase.

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* an InfinityX-21 MP digital camera mounted atop the microscope. Differential scanning calorimetry was performed on a Mettler DSC822<sup>e</sup> calibrated before use against indium and zinc standards under an atmosphere of dry nitrogen. DSC thermograms were processed in Matlab. Computational chemistry was performed using the using Gaussian G09 revision d01 on the York Advanced Research Computing Cluster (YARCC) as described in the text. [2]

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 K $\alpha$  ( $\lambda$  = 0.154056 nm) 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 and the data processed using Matlab. Raw data are available upon request from the University of York data catalogue.

The behaviour of materials under applied electric fields was studied as follows. The material in question was flow filled into a commercial antiparallel buffed polyimide cell (Linkam) constructed from ITO glass and with a spacing of approx.  $5 \pm 0.1 \mu m$ . Wires were affixed to the cells using indium metal, placing an upper temperature limit of 155 °C on measurements. A waveform was generated by a Hewlett Packard 33120A arbitrary waveform generator and amplified by a custom built QinetiQ linear x20 amplifier. The electrical response from the cell was amplified by a nano-current amplifier (20 k $\Omega$  or 100 k $\Omega$  impedance) and fed into a Hewlett Packard 54600B oscilloscope.

#### **1.2.** Synthetic Details and Chemical Characterisation



#### 1: 4-(9-(4-((4-cyanobenzoyl)oxy)phenyl)nonyl)phenyl 4-(pentyloxy)benzoate

A 5 ml reaction vial (Supelco) topped with a mininert valve was charged with 4-(9-(4-hydroxyphenyl)nonyl)phenyl 4-cyanobenzoate (50 mg, 113.4 µmol), 4-pentyloxybenzoic acid (47 mg, 226.7 µmol), EDAC (43 mg, 226.7 µmol), DMAP (3 mg) and anhydrous DCM (3 ml). The suspension was stirred under an atmosphere of dry nitrogen for 2 hours, until the complete consumption of 4-(9-(4-hydroxyphenyl)nonyl)phenyl 4-cyanobenzoate ( $Rf_{DCM} = 0.2$ ) and the formation of a new spot ( $Rf_{DCM} = 0.7$ ). The reaction mixture was purified by column chromatography with 1:1 DCM/hexanes as the eluent followed by recrystalisation from ethanol, affording the title compound as fine colourless crystals.

Yield: 52 mg (73%)

<sup>1</sup>H NMR (400 MHz, CDCI<sub>3</sub>): 8.29 (2H, ddd, 
$$J_{H-H} = 1.8$$
 Hz,  $J_{H-H} = 2.5$  Hz,  $J_{H-H} = 8.9$  Hz, ArH),  
8.10 (2H, ddd,  $J_{H-H} = 1.8$  Hz,  $J_{H-H} = 2.5$  Hz,  $J_{H-H} = 8.9$  Hz, ArH),  
7.79 (2H, ddd,  $J_{H-H} = 1.8$  Hz,  $J_{H-H} = 2.4$  Hz,  $J_{H-H} = 8.5$  Hz, ArH),  
7.21 (2H, ddd,  $J_{H-H} = 1.8$  Hz,  $J_{H-H} = 2.4$  Hz,  $J_{H-H} = 8.5$  Hz, ArH),  
7.16 - 7.00 (4H, m, ArH), 6.94 29 (2H, ddd,  $J_{H-H} = 1.8$  Hz,  $J_{H-H}$   
= 2.5 Hz,  $J_{H-H} = 8.9$  Hz, ArH), 4.02 (2H, t,  $J_{H-H} = 6.6$  Hz, ArO-  
CH<sub>2</sub>-CH<sub>2</sub>-), 2.73 - 2.56 (4H, m, Ar-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>7</sub>-CH<sub>2</sub>-Ar),1.87 -  
1.70 (2H, m, Ar-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>), 1.70 - 1.52 (4H, m, Ar-  
CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>5</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Ar), 1.51 - 1.19 (14H, m, ArO-  
(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> + Ar-(CH<sub>2</sub>)<sub>2</sub>-(CH<sub>2</sub>)<sub>5</sub>-(CH<sub>2</sub>)-Ar), 0.93 (3H, t,  
 $J_{H-H} = 6.9$  Hz, ArO-(CH<sub>2</sub>)<sub>4</sub>-CH\_3).

<sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, CDCl<sub>3</sub>): 165.33, 163.93, 163.62, 149.10, 148.57, 141.28, 140.48, 133.73, 132.55, 132.40, 130.79, 129.67, 129.45, 121.84, 121.59, 121.20, 118.09, 117.06, 114.41, 68.46, 35.55, 31.66, 31.62, 29.63, 29.45, 29.42, 29.40, 28.97, 28.31, 22.62, 14.20.

MS M/Z (ESI+): 654.3186 (calcd. for  $C_{41}H_{45}NNaO_5$ : 654.3190, M + Na)

Assay (HPLC, peak area): 99.2% (230/250 nm, RT = 12.0 min)

1.3. Tabulated Differential Scanning Calorimetry Data

	1	2	3	4	5	6	7	8	9	10	mean	SD
MP	81.41	81.40	81.43	81.41	81.50	81.42	81.43	81.42	81.43	81.43	81.43	0.02 7
'Х' - N <sub>тв</sub>	56.10	56.10	56.11	56.11	56.12	56.09	56.10	56.11	56.11	56.12	56.11	0.00 9
N <sub>тв</sub> — N	91.89	91.88	91.89	91.88	91.89	91.88	91.87	91.88	91.89	91.88	91.88	0.00 7
N - Iso	110.8 2	110.8 2	110.8 3	110.8 3	110.8 3	110.8 2	110.8 1	110.8 2	110.8 3	110.8 3	110.8 2	0.00 7

Table SI-1:Tabulated transition temperatures (°C) for compound 1 for each DSC cycle<br/>(obtained at 10 °C min<sup>-1</sup>) along with mean and standard deviations. Melting<br/>point (MP) data taken on heating, all other transitions taken on cooling cycles.

	1	2	3	4	5	6	7	8	9	10	mea n	SD
											35.8	0 19
MP	35.7 4	35.8 1	35.7 4	35.8 2	36.3 7	35.6 9	35.7 8	35.8 2	35.7 5	35.7 4	3	4
'X' -	10.2	10.2	10.2	10.2	10.3	10.3	10.2	10.2	10.2	10.3	10.3	0.00
N <sub>TB</sub>	9	9	9	9	1	0	9	9	9	0	0	4
<b>N</b> <sub>тв</sub> –	0.31	0.31	0.32	0.31	0.31	0.31	0.31	0.31	0.32	0.31	0.04	0.00
Ν											0.31	2
N -											0.04	0.00
lso	0.62	0.62	0.61	0.61	0.62	0.62	0.62	0.62	0.62	0.62	0.61	2

Table SI-2:Tabulated associated enthalpies of transition (kJ mol<sup>-1</sup>) for compound 1 for<br/>each DSC cycle (obtained at 10 °C min<sup>-1</sup>) along with mean and standard<br/>deviations. Melting point (MP) data taken on heating, all other transitions<br/>taken on cooling cycles.

	1	2	3	4	5	6	7	8	9	10	mea n	SD
MP	12.1 3	12.1 5	12.1 2	12.1 5	12.3 3	12.1 1	12.1 4	12.1 5	12.1 3	12.1 2	12.1 5	0.06 5
'Х' - N <sub>тв</sub>	3.76	3.76	3.76	3.76	3.76	3.76	3.76	3.76	3.76	3.76	3.76	0.00 1

<b>N</b> <sub>тв</sub> –											0 10	0.00	
Ν	0.10	0.10	0.11	0.10	0.10	0.10	0.10	0.10	0.11	0.10	0.10	1	
N -											0.10	0.00	
lso	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	1	

Table SI-3:Tabulated dimensionless associated entropies of transition (ΔS/R) for<br/>compound 1 for each DSC cycle (obtained at 10 °C min<sup>-1</sup>) along with mean<br/>and standard deviations. Melting point (MP) data taken on heating, all other<br/>transitions taken on cooling cycles.

# 1.4. Supplemental DSC Data



Figure SI-1: DSC thermograms of the first cool of compound 1 at a range of heat/cool rates (1 – 20 °C min). Expansions show (from left to right) the 'X' – N<sub>TB</sub> phase transition, the N<sub>TB</sub> - N phase transition and the N – Iso phase transition. In all cases the onset temperature and associated enthalpies of transition are effectively invariant with heat/cool rate, as discussed in the text.

## 1.5. Supplemental NMR spectra



**Figure SI-2:** <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) NMR spectra of compound **1**, with expansions showing the 'aliphatic' region (1.0 - 2.2 ppm) and the 'aromatic' region (6.7 - 8.5 ppm).



Figure SI-3:  ${}^{13}C{}^{1}H{}$  (100.5 MHz, CDCl<sub>3</sub>) NMR spectra of compound 1



# 1.6. Supplemental HPLC Chromatographs

**Figure SI-4:** HPLC chromatograph of compound **1** obtained with SiO<sub>2</sub> stationary phase, neat dichloromethane mobile phase, detector wavelengths of 230 nm and 250 nm, a flow rate of 1 ml min<sup>-1</sup> and an injection volume of 10 μl



**Figure SI-5:** RP-HPLC chromatograph of compound **1** obtained with C18 stationary phase, neat acetonitrile mobile phase, detector wavelengths of 230 nm and 250 nm, a flow rate of 1 ml min<sup>-1</sup> and an injection volume of 10 μl.

## 1.7. Supplemental Small-Angle X-ray Scattering Data

In order to collect of scattered X-rays at values of Q down to a lower limit of 0.06 Å<sup>-1</sup>, *i.e.* a d-spacing of  $\approx$  100 Å, the detector position was moved from 121 mm from the sample to 300 mm. This diffractometer configuration allows the recording of scattering at angles as small as around 0.8 ° theta, however, the ability to simultaneously record small-angle and wide-angle data is forfeited. Figure SI-5 presents SAXS data collected on the lower temperature mesophase of compound **1** at a temperature of 49 °C, along with a 5-term Gaussian fit and plotted residuals from the fit.



**Figure SI-6:** Top: plot of integrated scattered X-ray intensity (arbitrary units, blue circles) along with a 5-term Gaussian fit (dotted red line) for compound **1** in the lower temperature phase ('X') at 49 °C. Bottom: residuals from the fitting process.

Figure SI-6 presents SAXS data collected on twist-bend mesophase of compound **1** at a temperature of 58 °C, along with a 5-term Gaussian fit and plotted residuals from the fit. As discussed by Zhu, SAXS can be used to distinguish between the N<sub>TB</sub> and 'splay-bend modulated nematic' phase as the former has no modulation of electron density (and thus the nanoscale periodicity of the N<sub>TB</sub> does not lead to Bragg scattering in non-resonant SAXS.),  $2\pi$ 

however, the later does have EDM and therefore should give Bragg Scattering at  $P_{SB}$ , where  $P_{SB}$  is the periodicity of the splay-bend modulated phase. The absence of Bragg-scattering (other than the diffuse peak corresponding to the  $\frac{1}{2}$  molecular length at Q  $\approx$  0.33) in the phase directly below the nematic in compound **1** means this phase is most likely a twist-bend nematic. We note the remote possibility that the mesophase may be a splay-bend modulated phase with pitch of >10.5 nm, in which case the Bragg scattering will be observed at Q  $\leq$  0.06 Å<sup>-1</sup>, this being below the lowest value of Q we can measure using our present experimental setup. However, this is unlikely, as for such a modulated phase the presence of harmonics at would be expected to reveal the presence of such a peak.



Figure SI-7: Top: plot of integrated scattered X-ray intensity (arbitrary units, blue circles) along with a 5-term Gaussian fit (dotted red line) for compound 1 in the twistbend phase at 58 °C. Bottom: residuals from the fitting process.

#### 1.8. Gaussian Output Archive

N-N= 4.296544426562D+03 E-N=-1.328373264260D+04 KE= 2.001104195551D+03 1\1\GINC-RNODE10\FOpt\RB3LYP\6-31G(d)\C41H45N1O5\RM591\25-May-2016\0\\ # opt b3lyp/6-31g(d) nosymm geom=connectivity\\Title d\\0,1\C,frea Card Require 5.3356227425.3.2406173388.0.5604993046\C.-3.9458759893.3.348 6012007,0.5763516281\C,-3.3101744795,4.5758681512,0.3468692828\C,-4.11 44639781,5.6963957348,0.097281868\C,-5.505838618,5.6097959505,0.073360 0522\C,-6.1037421042,4.3741384844,0.3111342313\H,-5.8298053949,2.29105 3757,0.7409257\H,-3.3469379008,2.4629467776,0.7755263427\H,-3.64506800 25,6.6613980427,-0.0794498532\H,-6.1127493059,6.4874471088,-0.11196610 05\O,-7.4889639246,4.1802998292,0.2312862552\C,-8.3469251676,5.0016185 125.0.9010122944\O.-8.0067772619,5.9318797452,1.5961258439\C.-9.768085 7545,4.6051852137,0.6682223506\C,-10.1285738571,3.5374199019,-0.165471 401\C,-10.7612060589,5.3496831537,1.3196876839\C,-11.4692856549,3.2166 931963,-0.3473268668\H,-9.3584187641,2.9640925656,-0.6676320655\C,-12. 1025639598,5.0348272797,1.1445387462\H,-10.4604245455,6.1722995584,1.9 593634996\C,-12.4627297159,3.9643088886,0.3074875206\H,-11.7557788068, 2.3922700307,-0.9918937926\H,-12.875109357,5.6076167777,1.6467604807\C ,-13.846193961,3.634095913,0.1209102483\N,-14.9679016429,3.3660647299, 0.0305648862\C,-1.8003613352,4.6806139984,0.3267422003\H,-1.494932681 4,5.6696422246,0.6932346141\H,-1.3711588828,3.9465307189,1.0214710636\ C,-1.1965335016,4.4572529408,-1.0749215435\H,-1.5019908084,3.468084628 9.-1.4438101758\H,-1.6294763884,5.1880448685,-1.7723082576\C,0.3330503 59.4.5665061603.-1.0966126128\H.0.6318965219.5.5573057582.-0.723258108 5\H,0.7601071156,3.8363918617,-0.393033471\C,0.9397078166,4.3444348535 2.488308814\H,0.6409885864,3.3533578898,-2.8606817329\H,0.5111008239 ,5.073833412,-3.1914450893\C,2.4697760209,4.4549145848,-2.5135347996\H ,2.7681091224,5.4460671176,-2.1408014055\H,2.8982363955,3.7254884228,-1.8101368134\C,3.0769735484,4.233277705,-3.9050402433\H,2.7788326953,3 .2422849266,-4.2781123325\H,2.6489910904,4.962852793,-4.6083820836\C,4 .6070618689.4.343860103.-3.9291450691\H.4.9055366718.5.3344322528.-3.5 547441895\H,5.035375591,3.6133496741,-3.2266417227\C,5.2133522709,4.12 43157884,-5.3206846797\H,4.9215808783,3.1348832639,-5.6999334199\H,4.7 944829038,4.855306363,-6.02644394\C,6.7514901179,4.235465779,-5.334994 3855\H,7.0400169975.5.2239144413,-4.9532078769\H,7.1684553457,3.499615 7417,-4.634404278\C,7.3527391392,4.0261403111,-6.7083295867\C,7.521898

1149,5.0997828164,-7.5932165216\C,7.7242106813,2.7489759572,-7.1480184 265\C,8.0413438421,4.9200396973,-8.8745429851\H,7.24579746,6.102358311 4,-7.2738361265\C.8.2496061711,2.5488273447,-8.4236813588\H,7.60774403 78,1.8970009719,-6.4817577327\C,8.4067579058,3.6367018432,-9.279073671 4\H,8.1754766516,5.7625153498,-9.5415176648\H,8.5422839208,1.560398334 6,-8.7642002325\O.8.8641383353,3.352903107,-10.5662453629\C.9.88107846 73.4.0880277814.-11.125360742\0.10.4356657754.5.0058419133.-10.5604829 589\C,10.2044826426,3.6103243761,-12.489555078\C,9.5248921955,2.550828 8456,-13.1172546531\C,11.2396547679,4.2530515281,-13.1789470464\C,9.87 55507136.2.1522823246.-14.3968408494\H.8.7214196706.2.0448604514.-12.5 942207065\C,11.6018208273,3.8604729726,-14.4640344491\H,11.7598856078, 5.0697575534,-12.6890898572\C,10.9169998597,2.8027078808,-15.081953617 \H,9.3602824595,1.3371651601,-14.8949272072\H,12.4077380676,4.37615541 8,-14.9725364464\O,11.182111535,2.3361278971,-16.3288323924\C,12.23014 00036,2.9410168008,-17.0917222253\H,12.0183338249,4.0108905665,-17.230 4553727\H,13.1824814577,2.8518321014,-16.5496076463\C,12.3008783157,2. 2247899878,-18.4330438068\H,11.3235975648,2.3059060292,-18.925963175\H ,12.47430116,1.1563293997,-18.2514089154\C,13.3991603419,2.7910041498, 19.3420884554\H,13.2250741282,3.8648602415,-19.5057944431\H,14.372762 2995,2.71355261,-18.835875027\C,13.4802673919,2.0818824017,-20.7004093 226\H,12.5079623998,2.1600471529,-21.2066400214\H,13.653467959,1.00890 99137,-20.5376684103\C,14.5773190358,2.6459386743,-21.6085233151\H,14. 609540148,2.1190327834,-22.5687152943\H,14.4114033958,3.7098384658,-21 .8180142973\H,15.5660506877,2.5507375193,-21.143108979\\Version=EM64L-G09RevD.01\HF=-2020.3872427\RMSD=3.037e-09\RMSF=7.318e-07\Dipole=1.967 5352,-0.463094.-1.2724238\Quadrupole=-60.0031638.-1.7668086.61.7699724 ,3.7830669,-35.0732231,-3.3062228\PG=C01 [X(C41H45N1O5)]\\@

### 1.9. References

- R. J. Mandle and J. W. Goodby, "A Liquid Crystalline Oligomer Exhibiting Nematic and Twist-Bend Nematic Mesophases", *ChemPhysChem*, **2016**, 7, 967-970, DOI: 10.1002/cphc.201600038
- Gaussian 09, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.