Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary information for

A Twist-bend Nematic to an Intercalated, Anticlinic, Biaxial Phase Transition in Liquid Crystal Bimesogens

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1.1 General Methods.

Bis 1,9-(4-Hydroxyphenyl)nonane, was prepared as described previously. [1] 4′-Propylbiphenyl-4-carboxylic acid was purchased from Synthon Gmbh. 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. 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 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 (^{1}H NMR, ^{13}C NMR) homogenous material.

NMR spectra were recorded on a JEOL ECX spectrometer operating at 400 MHz (^{1}H), 100.5 MHz (^{13}C). FT-IR spectroscopy was performed using a Shimadzu IR Prestige-21 with Specac Golden Gate diamond ATR IR insert. High-performance liquid chromatography was performed on a Shimadzu Prominence modular HPLC system comprising a LC-20A quaternary solvent pump, a DGU-20A$_5$ degasser, a SIL-20A autosampler, a CBM-20A communication bus, a CTO-20A column oven, and a SPO-20A dual wavelength UV-vis detector operating at 230 and 255 nm. The column used was an Ascentis C18 bonded reversed phase silica column with a 5 μm pore size, an internal diameter of 4.6 mm and a length of 250 mm. In all cases the mobile phase was neat acetonitrile.

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 digital camera or a Sony NEX 5R mirrorless digital camera mounted atop the microscope. 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. Computational chemistry was performed using the using Gaussian G09 revision d01 on the York Advanced Research Computing Cluster (YARCC) as described in the text. [3]

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 (λ = 0.154056 nm) from a 1 μS microfocus source. Diffraction patterns were recorded on a 2048x2048 pixel Bruker VANTEC 500 area detector. 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 at http://dx.doi.org/10.15124/5c5f0442-a8a1-4dc8-acdf-bdf3b3070762

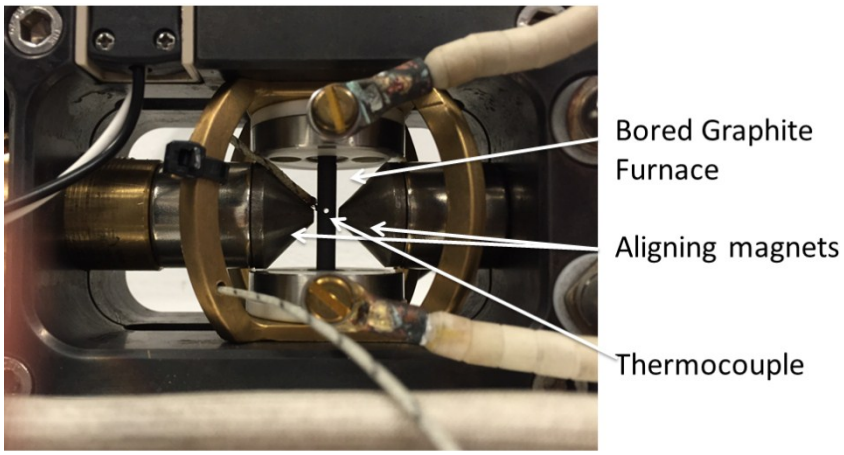
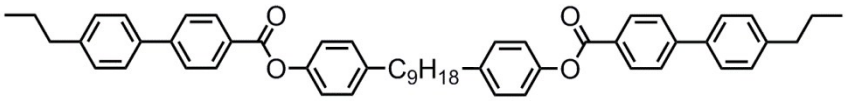


Figure SI1: Photograph of the custom built bored graphite rod furnace used to obtain SAXS data at non ambient temperatures.

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 ± 0.1 μm. 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 kΩ or 100 kΩ impedance) and fed into a Hewlett Packard 54600B oscilloscope.



Nonane-1,9-diyl*bis*(4,1-phenylene) bis(4'-propyl-[1,1'-biphenyl]-4-carboxylate) 9-(3BEP)2

A suspension of *bis* 1,9-(4-Hydroxyphenyl)nonane (312 mg, 1 mmol), 4′-propylbiphenyl-4-carboxylic acid (720 mg, 3 mmol), EDAC (3 mmol) and DMAP (25 mg) in dry dichloromethane (5 ml) was stirred until complete consumption of *bis* 1,9-(4-Hydroxyphenyl)nonane as evidenced by TLC (< 2 h). The crude material was purified by dry vacuum flash chromatography [4, 5] with a gradient of DCM/hexanes as the eluent, followed by recrystalisation from ethanol/THF (5:1) to yield the target compounds as a fine white solid.

Yield: 490 mg, 64.7%

^{1}H NMR (400 MHz, $CDCl_3$): 0.91 (6H, t, J = 7.0 Hz, $C\underline{H_3}$-CH_2-CH_2-Ar), 1.20 – 1.32 (10H, m, Ar-CH_2-CH_2-$(\underline{CH_2})_5$-CH_2-Ar, 1.50 – 1.68 (8H, m, Ar-CH_2-$\underline{CH_2}$-CH_3 + Ar-CH_2-$\underline{CH_2}$-$(CH_2)_5$-$\underline{CH_2}$-CH_2-Ar), 2.52 – 2.61 (8 H, m [2x t] Ar-$\underline{CH_2}$-CH_2-CH_3 + Ar-$\underline{CH_2}$-CH_2), 7.05 (4H, ddd, *J* = 1.8 Hz, *J* = 2.8 Hz, *J* = 8.5 Hz, Ar*H*), 7.16 (4H, ddd, *J* = 1.8 Hz, *J* = 2.8 Hz, *J* = 8.5 Hz, Ar*H*), 7.22 (4H, ddd, *J* = 1.8 Hz, *J* = 2.1 Hz, *J* = 8.2 Hz, Ar*H*), 7.50 (4H, ddd, *J* = 1.8 Hz, *J* = 2.1 Hz, *J* = 8.2 Hz, Ar*H*), 7.63 (4H, ddd, *J* = 1.8 Hz, *J* = 1.8 Hz, *J* = 8.5 Hz, Ar*H*), 8.17 (4H, ddd, *J* = 1.8 Hz, *J* = 1.8 Hz, *J* = 8.5 Hz, Ar*H*)

^{13}C NMR (100.5 MHz, $CDCl_3$): 165.44, 149.00, 146.31, 143.22, 140.64, 137.33, 130.79, 129.48, 129.25, 128.20, 127.28, 127.09, 121.48, 37.85, 35.53, 31.62, 29.60, 29.46, 29.43, 24.66, 14.01.

FT-IR (νmax, cm^{-1}): 692, 727, 761, 823, 875, 1004, 1016, 1076, 1165, 1190, 1265, 1398, 1465, 1506, 1604, 1726, 2848, 2916

MS (ESI+, m/z): 779.4033 (100%, $C_{53}H_{56}NaO_4$, calcd. for $C_{53}H_{56}NaO_4$ 779.4071, M + Na)

Assay (RP-HPLC): > 99%

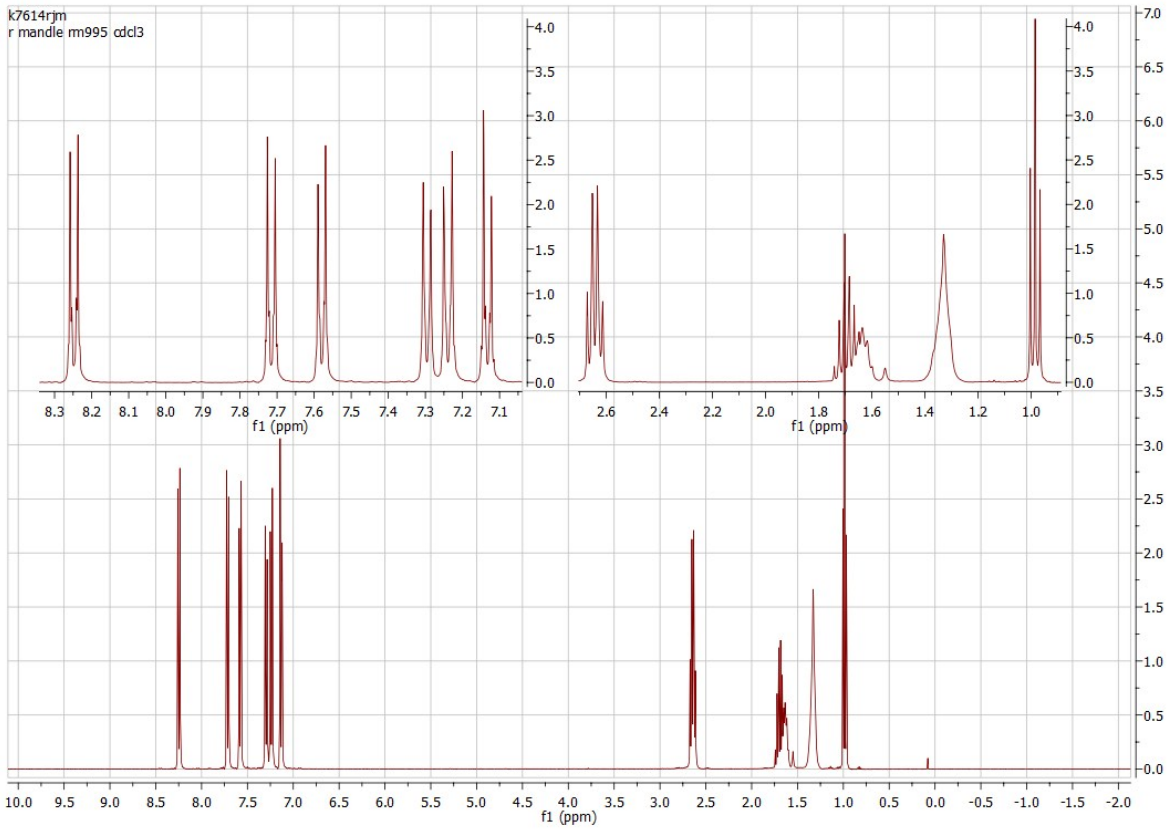


Figure SI2: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **9-(3BEP)2**, with expansions of the aromatic (top left) and aliphatic regions (top right)

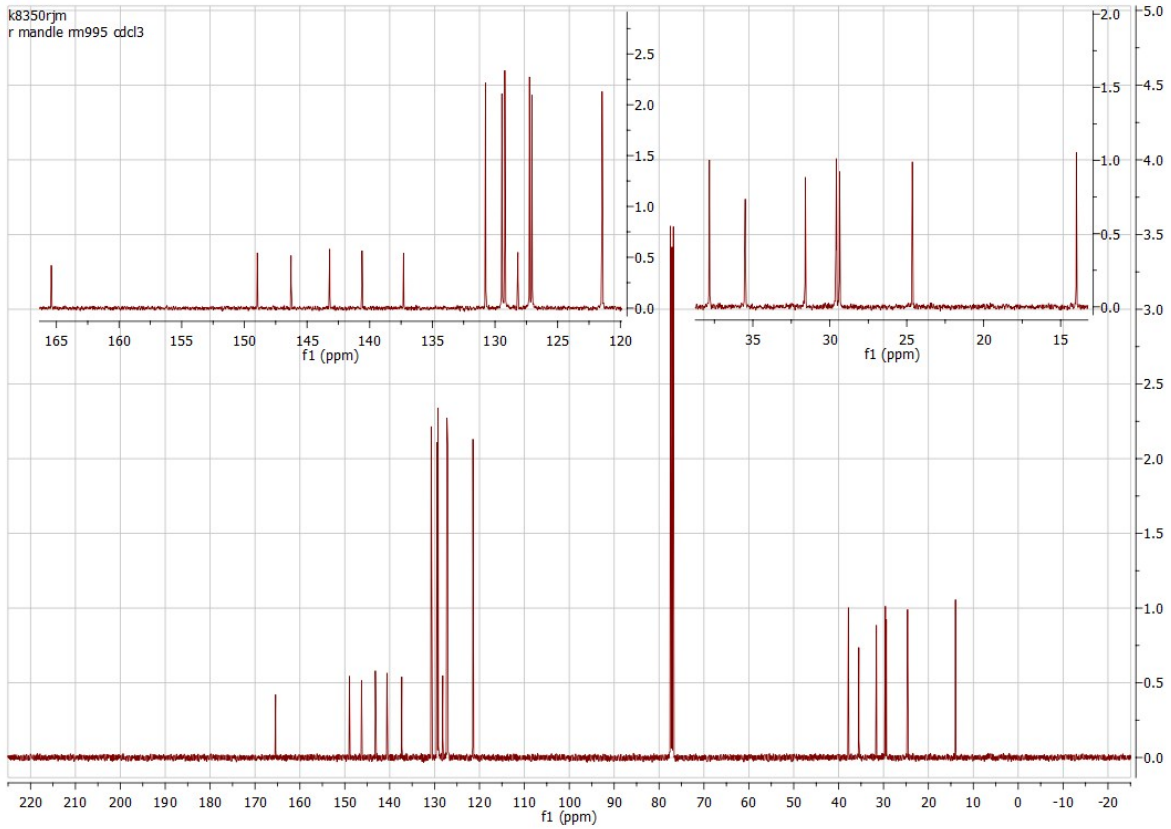


Figure SI3: ^{13}C NMR spectra (100.5 MHz, $CDCl_3$) of **9-(3BEP)2**

References

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

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