Electronic Supplementary Information

Molecular Topology of Three Ring Nematogens from ^{13}C-^{1}H Dipolar Couplings

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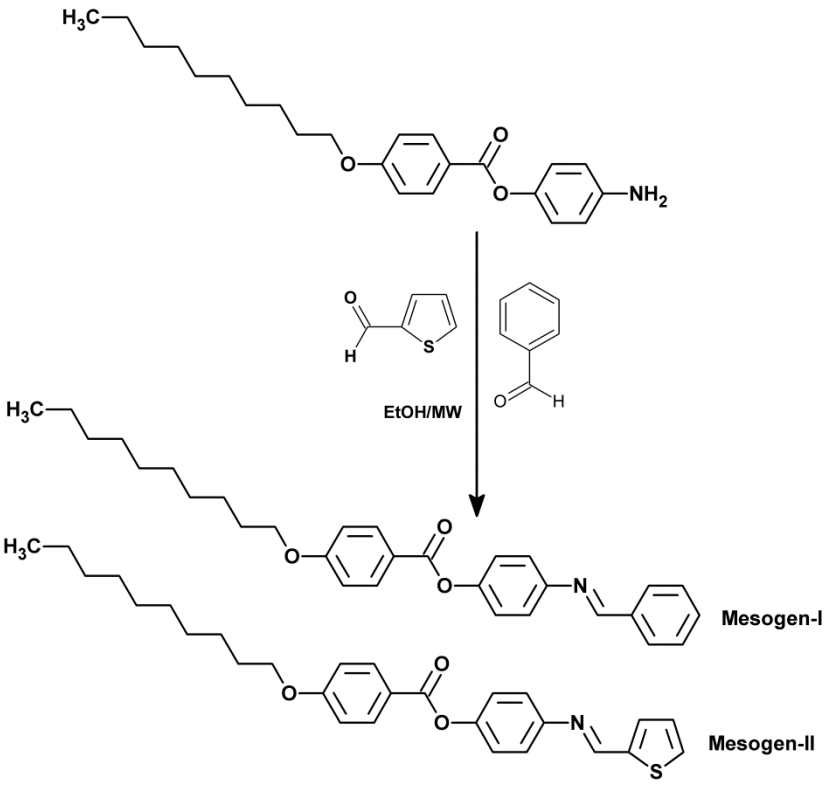


Scheme -1

Scheme-1 shows the strategy adopted for synthesising Mesogens 1 and II. The synthesis of 4-decyloxy benzoyloxy aniline was accomplished by the protocols reported in our earlier publications.[1-3] The spectral data of the amine is consistent with its molecular structure. The Mesogen II was earlier reported by Nugent et al. [4] and the spectral data is given below.

Synthesis of Mesogen I/II

In a typical experiment, equimolar quantities of 4-decyloxy benzoyloxy aniline ( ) and benzaldehyde or 2-thiophene carboxaldehyde were taken in 100 ml conical flask. Few drops of ethanol were added to the flask to make the contents wet. Then the flask was kept in commercial microwave oven (power 40 W) for 15 mts. After that solid obtained was washed with excess methanol and was filtered. The solid obtained was purified with recrystallization from acetonitrile/methanol.

Mesogen I

Yield: 70%, m.p.- FT-IR (KBr, cm^{-1}): 3070 (aromatic C-H_{str}), 2920, 2849 (C-H_{str}), 1727 (C=O_{str}), 1605, 1577, 1511 (C=C_{str} aromatic), 1469 (C-H_{ben}), 1257,1200 (C-O-C $_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm ($CDCl_3$): δ8.48 (s, 1H,-CH=N), 8.15 (d, 2H, Ar-H), 7.91 (m, 2H, Ar-H), 7.48 (d, 3H, Ar-H), 7.26 (m, 4H, Ar-H), 6.97 (d, 2H, Ar-H), 4.04 (t, 2H, O-CH_2), 1.82(m, 2H, CH_2), 1.29-1.51(m, 14H, CH_2), 0.89(t, 3H, CH_3); ^{13}C-NMR ppm ($CDCl_3$):δ 165.1, 163.6, 160.5, 149.6, 149.3, 136.2, 132.3, 131.5, 128.9, 128.9, 122.5, 121.9, 121.5, 114.4, 68.4, 31.9, 29.6, 29.4, 29.3, 29.1, 26.0, 22.7 and 14.1

Mesogen II

Yield: 67.2%, m.p-103 °C, FT-IR (KBr, cm^{-1}): 3098, 3070 (aromatic C-H_{str}), 2915, 2846 (C-H_{str}), 1725 (C=O_{str}), 1606, 1508 (C=C_{str} aromatic), 1468, 1423(C-H_{ben}), 1264,1199,1186 (C-O-C $_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm ($CDCl_3$): δ8.58 (s, 1H,-CH=N), 8.15 (d, 2H, Ar-H), 7.51 (dd, 1H, Thio-H)7.49 (dd, 1H, Thio-H), 7.27-7.20 (m, 4H, Ar-H), 7.14 (dd, 1H, Thio-H),6.96 (d, 2H, Ar-H), 4.03 (t, 2H, O-CH_2), 1.81(m, 2H, CH_2), 1.47(m, 14H, CH_2), 0.88(t, 3H, CH_3); ^{13}C-NMR ppm ($CDCl_3$):δ165.0, 163.5, 153.0, 149.2, 148.9, 142.7, 132.3, 132.2, 130.4, 127.7, 122.57, 122.4, 121.9, 121.5, 114.3, 68.3, 32.1, 29.6, 29.5, 29.4, 29.3, 26.0, 22.7 and 14.1.

SAMPI-4 pulse sequence:

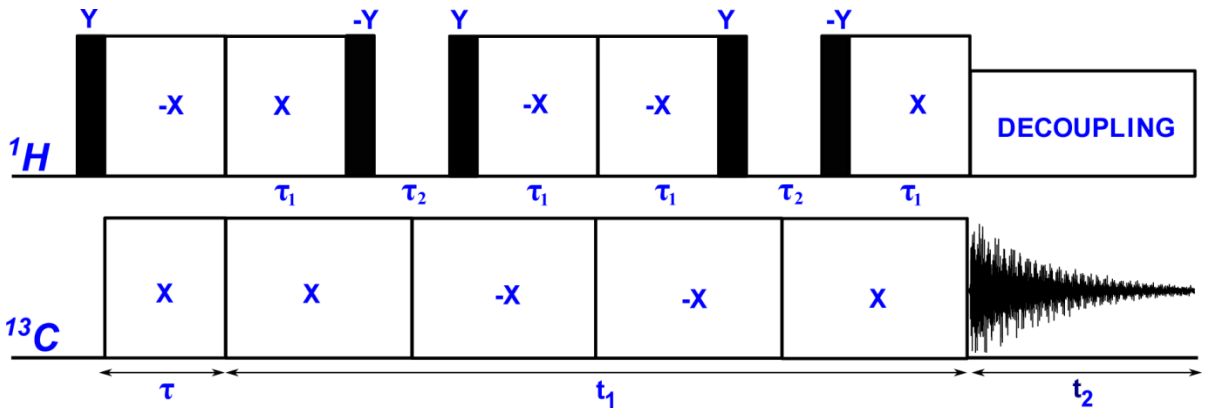


Figure S1: Measurement of ^{13}C-^{1}H Dipolar Couplings using SAMPI-4[5] pulse sequence a variant of Separated Local Field (SLF) experiment. The method yields a 2D spectrum with carbon chemical shifts along the F_2 dimension and the proton-carbon dipolar oscillation frequencies along the F_1 dimension. Here τ is CP contact time and the darker boxes represent 90° pulses

HOPM Images:

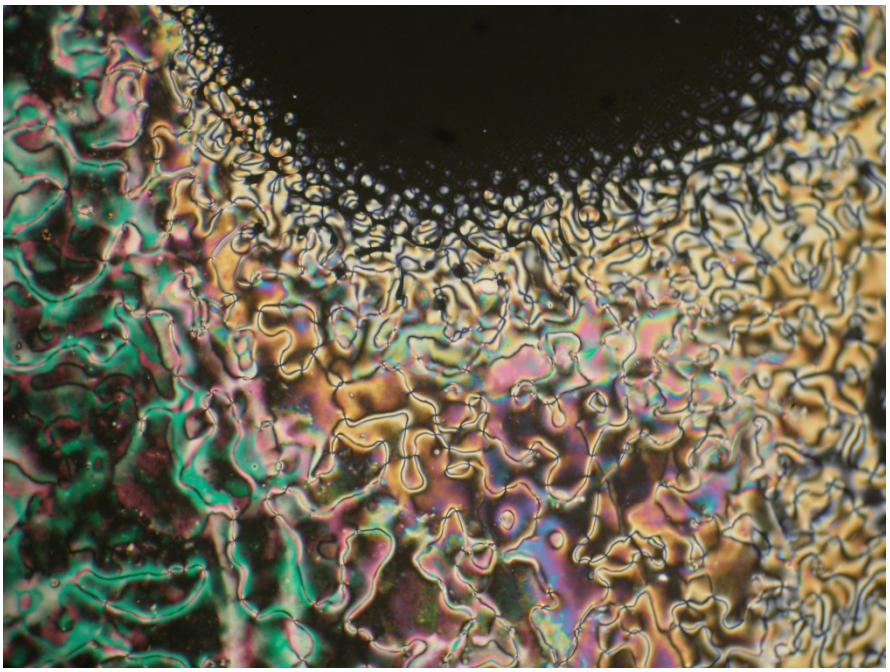


Figure S2: Mesogen I on cooling from isotropic phase exhibiting nematic texture at 133.5°C

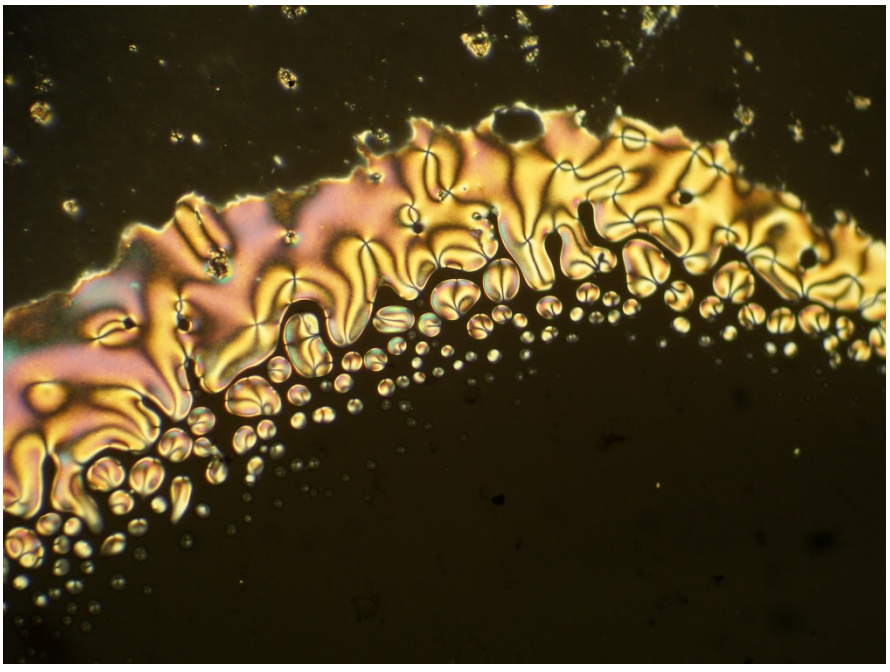
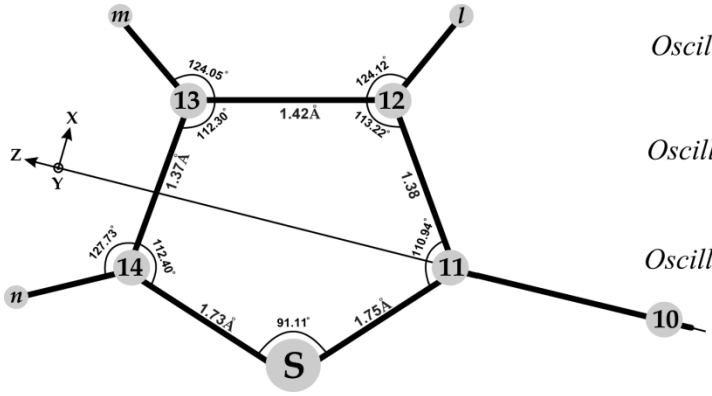


Figure S3: Mesogen II on cooling from isotropic phase showing nematic phase at 121.9°C

Thiophene Model for Order Parameter Calculation

Figure S4 shows thiophene model is utilized for calculating the orientational order parameter of thiophene for Mesogen II from the experimental dipolar oscillation frequencies. The model also enabled the assignment of the spectral lines by matching calculated dipolar couplings to experimental values obtained from the 2D SAMPI-4 spectrum. The bond angles and bond lengths of thiophene ring are used from energy optimized structures of mesogens from quantum chemical calculations.



$$Oscillation\ Frequency,\ f_{12}=(D_{12l}^2+D_{12m}^2+D_{12n}^2)^{1/2}$$

$$Calculate,\ |f_{12}-f_{12}^{exp}|^2$$

$$Oscillation\ Frequency,\ f_{13}=(D_{13m}^2+D_{13l}^2+D_{13n}^2)^{1/2}$$

$$Calculate,\ |f_{13}-f_{13}^{exp}|^2$$

$$Oscillation\ Frequency,\ f_{14}=(D_{14n}^2+D_{14m}^2+D_{14l}^2)^{1/2}$$

$$Calculate,\ |f_{14}-f_{14}^{exp}|^2$$

Figure S4: Thiophene model to calculate orientational order parameter.

References

1) T. Narasimhaswamy and K. S. V. Srinivasan, *Liq. Cryst*. 2004, **31**, 1457−1462.

2) S. Kalaivani, T. Narasimhaswamy, B. B. Das , N. P. Lobo and K. V. Ramanathan, *J. Phys. Chem. B*, 2011, **115**, 11554−11565.

3) T. Narasimhaswamy, N. Somanathan, D. K. Lee and A. Ramamoorthy, *Chem. Mater.* 2005, **17**, 2013-2018.

4) S. J. Nugent, Q. M. Wang and D. W. Bruce, *New. J. Chem.*, 1996, **20**, 669-675.

5) A. A. Nevzorov and S. J. Opella, *J. Magn. Reson.* 2007, **185**, 59−70.