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**The impact of molecular symmetry and shape on the
stability of discotic liquid crystals**

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2 crystals

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Abstract

Three series of dibenzo[a,c]phenazines were prepared in an order to assess the impact of side chain position on the phase stability of columnar liquid crystals. Each series was composed of four isomeric compounds differing only in the disposition of hexyloxy and decyloxy chains around the central aromatic core, giving rise to electronically similar compounds with varying shapes and symmetries. The substitution pattern was found to have a moderate effect on the clearing transition of the liquid crystal, but a larger impact on the melting temperatures. These observations suggest a viable strategy for controlling the phase range of liquid crystals via judicious choice of peripheral chain structure and location.

Introduction

The unique ability of liquid crystals (LCs) to simultaneously exhibit both order and fluidity has been exploited in an enormous variety of applications, including display devices,^{1,2} holography,³ biosensors^{4,5} and photoactuators.^{6,7} Recently, discotic liquid crystals (DLCs) have emerged as promising organic semiconductors for use in solar cells, OLEDs and field effect transistors.^{8,9} Because the usefulness of an LC for any given application is limited by its phase stability, identifying the factors that control temperature ranges of these DLCs remains an important and ongoing challenge.¹⁰⁻²⁰

1 In the case of the disc-shaped molecules that form semiconducting columnar phases,
2 a useful strategy for controlling liquid crystal phase ranges relies on modifying the
3 flexible chains that surround the central aromatic core, as transition temperatures
4 strongly depend upon the length, branching and pendant functional groups of these
5 chains.^{14, 21-22} Although mesogens generally possess multiple identical chains, it is
6 also possible, albeit synthetically more challenging, to construct discs with two or
7 more distinct chains, such as the dicyanodibenzoquinoxalines **CN-Q(w,x|y,z)**
8 previously prepared in our lab.³³ Such mixed chain systems have the capacity for
9 considerable structural diversity: even two pairs of alkyl groups (C₆H₁₃ and C₁₀H₂₁)
10 can generate four possible regioisomers. Each of these compounds exhibited distinct
11 transition temperatures, enabling us to control phase ranges by altering how groups
12 are disposed around the central core.

13
14 **INSERT STRUCTURE 1 HERE**
15

16 Although dramatic changes in phase behavior often accompany shuffling of side
17 chains, the underlying factors that govern these differences remain unclear.²³⁻³¹ Our
18 preliminary studies suggested that molecular symmetry has a marked effect on the
19 melting temperature, but has little impact on the LC-to-isotropic (clearing)
20 transition.^{16,32,33} In order to explore these structure property relations in more
21 detail, we prepared a series of dibenzophenazines **A(m)Q(w,x|y,z)**, derived from
22 the condensation of the corresponding o-phenylenes **A(m)** and quinones **Q(w,x|y,z)**
23 (Scheme 1). Starting from three diamines (m = 6, 8, 10) and three quinones, we were

able to readily obtain nine new discotic mesogens, comprising three families of isomers. For comparison, we also discuss the properties of the three dibenzophenazines **A(m)Q(6,6|10,10)** that were synthesized for previous studies.³²

INSERT SCHEME 1 HERE

Scheme 1. Synthesis of dibenzophenazines **A(m)Q(w,x|y,z)**.

Experimental

Instrumental

NMR spectra were obtained at 400 MHz or 600 MHz for ¹H-NMR, and 100 MHz or 150 MHz for ¹³C-NMR spectra were obtained on Bruker Advance instruments, as specified. Chemical shifts (δ) are expressed in ppm relative to the CDCl₃ solvent peak (δ = 7.26 ppm). Mass spectrometry was performed by MALDI-TOF on a Perspective Voyager-DE STR from PE Applied Biosystems using a nitrogen laser (337 nm) to desorb the analytes from the 2,5-dihydroxybenzoic acid matrix. High Resolution Mass Spectrometry (HR-MS) was performed on an Agilent 6210 TOF LC-MS with electrospray ionization (ESI). Elemental analyses were performed by Mr. Miki Yang and Mr. Frank Haftbaradaran at Simon Fraser University using a EA1110 CHN CE Instrument with WO₃ as accelerant.

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC 7 and the values for the temperatures and enthalpies of transition were recorded on the first heating/cooling cycle at a rate of 5 °C/min. Polarized optical microscopy

1 was performed using an Olympus BX50 polarized optical microscope equipped with
2 a Linkam LTS350 heating stage. Variable temperature X-ray diffraction experiments
3 were performed using Rigaku RAXIS rapid diffractometer with a Cu K α radiation, a
4 graphite monochromator and a Fujifilm Co. Ltd. curved image plate (460 mm x 256
5 mm). Samples were loaded into capillaries (~1 mm diameter) from the isotropic
6 phase and were heated using a home-made capillary furnace. `

7 **Materials**

8 Chemicals were used as purchased unless otherwise noted. Nitrogen gas was
9 purchased from Praxair. SnCl₂ and CDCl₃ was purchased from Aldrich.
10 Dichloromethane, hexanes, and ethyl acetate were purchased from VWR. NaCl,
11 MgSO₄, NaOAc, methanol, and HCl_(aq) were purchased from Caledon Laboratories
12 Ltd. Ethanol was obtained from Commercial Alcohols Inc. Silica (230-400 mesh) and
13 TLC plates were purchased from Silicycle Inc.

14 **Synthesis**

15 *General procedure for preparation of A(m)Q(w,x/y,z):* 4,5-dialkoxyl-phenylene-1,2-
16 diamines were obtained from catechol as previously reported.³² Due to the
17 instability of these compounds, they were isolated as their hydrochloride salts and
18 used immediately. The final compounds were obtained as bright yellow solids in
19 yields varying between 32-78%.

20 In a typical procedure, the 1,2-dialkoxy-4,5-dinitrobenzene (0.81 mmol) was
21 reduced to its diamine by heating at 80 °C in 25 mL ethanol in the presense SnCl₂

(5.7 mmol) and concentrated HCl (4 mL) for 8 hours. The solution was cooled to room temperature, poured over concentrated HCl (60 mL). The precipitate was filtered, washed with water and air-dried. The solid was immediately mixed with 2,3,6,7-tetrakis-alkoxy-phenanthrene-9,10-dione (0.15 mmol) and sodium acetate (3.0 mmol) in anhydrous ethanol (50 mL). The mixture was heated at reflux overnight. The mixture was cooled to RT, water (50 mL) was added and the mixture was extracted with DCM (3x40 mL). The organic phases were combined and washed with water (2x100 mL) and brine (100 mL). The solution was dried over MgSO_4 , filtered and evaporated. The product was purified by column chromatography (silica gel, 92:8 hexanes/ethyl acetate) to afford a yellow solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$.

A(6)Q(10,6/6,10) 1,2-Dihexyloxy-4,5-dinitrobenzene: 0.328 g, 0.890 mmol; 2,7-didecyloxy-3,7-dihexyloxy-phenanthrene-9,10-dione: 0.110 g, 0.153 mmol; Final product: 0.083 g, 0.0838 mmol, 55 %; ^1H NMR (CDCl_3 , 600 MHz) δ 0.87-0.90 (m, 6H), 0.93-0.95 (m, 12H), 1.25-1.46 (m, 40H), 1.56-1.62 (m, 12H), 1.94-2.01 (m, 12H), 4.27 (t, 8H, $J = 6.6$ Hz), 4.34 (t, 4H, $J = 6.6$ Hz), 7.53 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 14.03, 14.05, 14.11, 22.62, 22.66, 22.69, 25.76, 25.82, 26.19, 28.91, 29.36, 29.38, 29.50, 29.61, 29.68, 31.58, 31.69, 31.92, 69.05, 69.11, 69.66, 106.51, 106.75, 107.98, 124.21, 125.67, 139.12, 139.46, 149.35, 150.98, 152.75 (1 carbon signal missing/overlapping); MALDI-TOF for $[\text{C}_{64}\text{H}_{100}\text{O}_6\text{N}_2\text{-H}]^+$ calculated (found): 993.766 (993.773); Elemental analysis (%) for $[\text{C}_{64}\text{H}_{100}\text{O}_6\text{N}_2]$ calculated (found): C, 77.37 (76.99); H, 10.15 (10.10); N, 2.82 (3.06).

1 **A(6)Q(6,10/10,6)** 1,2-Dihexyloxy-4,5-dinitrobenzene: 0.345 g, 0.937 mmol; 3,6-
2 didecyloxy-2,7-dihexyloxy-phenanthrene-9,10-dione: 0.106 g, 0.147 mmol; Final
3 product: 0.114 g, 0.115 mmol, 78 %; ^1H NMR (CDCl_3 , 600 MHz) δ 0.88-0.90 (m, 6H),
4 0.93-0.96 (m, 12H), 1.29-1.46 (m, 40H), 1.55-1.64 (m, 12H), 1.93-2.02 (m, 12H), 4.27
5 (t, 8H, J = 6.6 Hz), 4.35 (t, 4H, J = 6.6 Hz), 7.52 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H); ^{13}C
6 NMR (CDCl_3 , 150 MHz) δ 14.02, 14.04, 14.10, 22.62, 22.67, 22.69, 25.77, 25.85, 26.17,
7 28.92, 29.30, 29.37, 29.43, 29.54, 29.61, 29.68, 31.58, 31.67, 31.92, 69.08, 69.13,
8 69.69, 106.57, 106.79, 108.05, 124.24, 125.70, 139.14, 139.48, 149.37, 151.01,
9 152.77; MS-ESI for $[\text{C}_{64}\text{H}_{100}\text{N}_2\text{O}_6\text{-H}]^+$ calculated (found): 993.77 (993.76); Elemental
10 Analysis (%) for $[\text{C}_{64}\text{H}_{100}\text{N}_2\text{O}_6]$ calculated (found): C, 77.37 (77.33); H, 10.15
11 (10.09); N, 2.82 (3.07);

12 **A(6)Q(6,10/6,10)** 1,2-Hexyloxy-4,5-dinitrobenzene: 0.3445 g, 0.935 mmol; 2,6-
13 didecyloxy-3,7-dihexyloxy-phenanthrene-9,10-dione: 0.113 g, 0.157 mmol; Final
14 product: 0.0570 g, 0.574 mmol, 37 %; ^1H NMR (CDCl_3 , 400 MHz) δ 0.87-0.90 (t, 6H, J
15 = 6.8 Hz), 0.92-0.96 (t, 12H, J = 7.2 Hz), 1.29-1.44 (m, 40 H), 1.55-1.62 (m, 12 H),
16 1.93-2.02 (m, 12 H), 4.27 (t, 8H, J = 6.6 Hz), 4.35 (t, 4 H, J = 6.6 Hz), 7.53 (s, 2 H), 7.77
17 (s, 2H), 8.76 (s, 2 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.02, 14.05, 14.07, 14.10, 22.61,
18 22.66, 22.67, 25.76, 25.82, 25.85, 26.16, 26.19, 28.91, 29.30, 29.37, 29.42, 29.50,
19 29.53, 29.60, 29.67, 31.58, 31.67, 31.69, 31.92, 69.06, 69.07, 69.12, 69.685, 69.690,
20 69.70, 106.57, 106.78, 106.80, 108.03, 108.04, 124.23, 124.26, 125.69, 139.14,
21 139.48, 139.54, 139.55, 151.01, 152.76 (15 carbon signals missing/overlapping);
22 MS-ESI for $[\text{C}_{64}\text{H}_{100}\text{N}_2\text{O}_6\text{-H}]^+$ calculated (found): 993.77 (993.76) ; Elemental

1 Analysis (%) for $[C_{64}H_{100}N_2O_6]$ calculated (found): C, 77.37 (77.20); H, 10.15
2 (10.14); N, 2.82 (3.02).

3 ***A(8)Q(10,6/6,10)*** 1,2-Dioctyloxy-4,5-dinitrobenzene: 0.345 g, 0.811 mmol; 2,7-
4 didecyloxy-3,7-dihexyloxy-phenanthrene-9,10-dione: 0.100 g, 0.139 mmol; Final
5 product: 0.0978 g, 0.0932 mmol, 67 %; 1H NMR ($CDCl_3$, 600 MHz) δ 0.87-0.92 (m,
6 12H), 0.93-0.95 (m, 6H), 1.28-1.46 (m, 48H), 1.56-1.63 (m, 12H), 1.94-2.01 (m, 12H),
7 4.27 (t, 8H, $J = 6.6$ Hz), 4.35 (t, 4H, $J = 6.6$ Hz), 7.53 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H);
8 ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.06, 14.11, 22.66, 22.68, 22.69, 25.82, 26.10, 26.19,
9 28.95, 29.29, 29.36, 29.38, 29.50, 29.61, 29.68, 31.69, 31.83, 31.92, 69.06, 69.12,
10 69.67, 106.76, 107.99, 124.22, 125.68, 139.13, 139.47, 149.36, 150.98, 152.75 (4
11 carbon signals missing/overlapping); MALDI-TOF for $[C_{68}H_{108}N_2O_6]$ calculated
12 (found): 1048.821 (1048.820); Elemental Analysis (%) for $[C_{68}H_{108}N_2O_6]$ calculated
13 (found): C, 77.81 (77.79); H, 10.37 (10.21); N, 2.67 (2.42).

14 ***A(8)Q(6,10/10,6)*** 1,2-Dioctyloxy-4,5-dinitrobenzene: 0.545 g, 1.28 mmol; 3,6-
15 didecyloxy-2,7-dihexyloxy-phenanthrene-9,10-dione: 0.118 g, 0.163 mmol; Final
16 product: 0.0545 g, 0.0519 mmol, 32 %; 1H NMR ($CDCl_3$, 600 MHz) δ 0.87-0.92 (m,
17 12H), 0.95 (t, 6H, $J = 6.9$ Hz), 1.26-1.46 (m, 46H), 1.55-1.63 (m, 16H), 1.94-2.01 (m,
18 12H), 4.27 (t, 8H, $J = 6.6$ Hz), 4.35 (t, 4H, $J = 6.6$ Hz), 7.52 (s, 2H), 7.77 (s, 2H), 8.76 (s,
19 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.07, 14.11, 22.67, 22.68, 22.69, 25.84, 26.09,
20 26.17, 28.95, 29.29, 29.37, 29.42, 29.53, 29.60, 29.68, 31.67, 31.83, 31.92, 69.06,
21 69.12, 69.66, 106.49, 106.76, 107.98, 124.21, 125.67, 139.13, 139.46, 149.34, 150.98,
22 152.74 (3 carbon signals missing/overlapping); MS-ESI for $[C_{68}H_{108}N_2O_6-H]^+$

1 calculated (found): 1049.8286 (1049.8228); Elemental Analysis (%) for
2 $[C_{68}H_{108}N_2O_6]$ calculated (found): C, 77.81 (77.33); H, 10.37 (10.36); N, 2.67 (3.11).

3 ***A(8)Q(6,10/6,10)*** 1,2-Dioctyloxy-4,5-dinitrobenzene: 0.3491 g, 0.822 mmol; 3,6-
4 didecyloxy-2,7-dihexyloxy-phenanthrene-9,10-dione: 0.113 g, 0.157 mmol; Final
5 product: 0.0932 g, 0.0888 mmol, 57 %; 1H NMR ($CDCl_3$, 400 MHz) δ 0.87-0.96 (m, 18
6 H), 1.25-1.45 (m, 48 H), 1.54-1.65 (m, 12 H), 1.93-2.02 (m, 12 H), 4.27 (t, 8H, J = 6.6
7 Hz), 4.35 (t, 4 H, J = 6.4 Hz), 7.53 (s, 2 H), 7.77 (s, 2H), 8.35 (s, 2 H); ^{13}C NMR ($CDCl_3$,
8 100 MHz) δ 14.05, 14.07, 14.10, 22.66, 22.67, 22.68, 22.69, 25.83, 25.85, 26.10,
9 26.17, 26.20, 28.96, 29.29, 29.30, 29.37, 29.50, 29.53, 29.61, 29.68, 31.67, 31.69,
10 31.83, 31.92, 69.09, 69.13, 69.70, 69.71, 106.57, 106.80, 108.065, 108.073, 124.25,
11 124.26, 125.49, 125.70, 139.15, 139.49, 149.38, 149.40, 149.51, 151.01, 151.02,
12 152.77 (12 carbon signals missing/overlapping); MS-ESI for $[C_{68}H_{108}N_2O_6-H]^+$
13 calculated (found): 1049.83 (1049.81); Elemental Analysis (%) for $[C_{68}H_{108}N_2O_6]$
14 calculated (found): C, 77.81 (77.71); H, 10.37 (10.28); N, 2.67 (3.07).

15 ***A(10)Q(10,6/6,10)*** 1,2-Didecyloxy-4,5-dinitrobenzene: 0.408 g, 0.850 mmol; 2,7-
16 didecyloxy-3,7-dihexyloxy-phenanthrene-9,10-dione: 0.108 g, 0.150 mmol; Final
17 product: 0.0637 g, 0.0576 mmol, 42 %; 1H NMR ($CDCl_3$, 600 MHz) δ 0.87-0.90 (m,
18 12H), 0.93-0.95 (m, 6H), 1.26-1.46 (m, 56H), 1.56-1.62 (m, 12H), 1.94-2.01 (m, 12H),
19 4.27 (t, 8H, J = 6.6 Hz), 4.35 (t, 4H, J = 6.6 Hz), 7.53 (s, 2H), 7.77 (s, 2H), 8.76 (s, 2H);
20 ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.06, 14.12, 22.66, 22.69, 25.82, 26.10, 26.19, 28.96,
21 29.36, 29.38, 29.42, 29.50, 29.59, 29.61, 29.64, 29.68, 31.69, 31.92, 69.06, 69.12,
22 69.67, 106.52, 106.77, 107.99, 124.23, 125.68, 139.14, 139.47, 149.36, 150.99,
23 152.76 (5 carbon signals missing/overlapping); MALDI-TOF for $[C_{72}H_{116}N_2O_6-H]^+$

1 calculated (found): 1105.891 (1105.900); Elemental Analysis (%) for $[C_{72}H_{116}N_2O_6]$
2 calculated (found): C, 78.21 (78.14); H, 10.57 (10.45); N, 2.53 (2.32).

3 ***A(10)Q(6,10/10,6)*** 1,2-Didecyloxy-4,5-dinitrobenzene: 0.437 g, 0.910 mmol; 3,6-
4 didecyloxy-2,7-dihexyloxy-phenanthrene-9,10-dione: 0.107 g, 0.149 mmol; Final
5 product: 0.0584 g, 0.0528 mmol, 36 %; 1H NMR ($CDCl_3$, 600 MHz) δ 0.89 (t, 12H, J =
6 6.8 Hz), 0.95 (t, 6H, J = 7.2 Hz), 1.29-1.45 (m, 56H), 1.54-1.64 (m, 12H), 1.93-2.02 (m,
7 12H), 4.27 (t, 8H, J = 6.6 Hz), 4.35 (t, 4H, J = 6.6 Hz), 7.52 (s, 2H), 7.77 (s, 2H), 8.76 (s,
8 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.05, 14.09, 22.67, 22.69, 25.86, 26.11, 26.18,
9 28.98, 29.32, 29.36, 29.37, 29.42, 29.46, 29.54, 29.59, 29.61, 29.64, 29.68, 31.68,
10 31.92, 69.12, 69.15, 69.74, 106.67, 106.85, 108.17, 124.29, 125.73, 139.16, 139.50,
11 149.41, 151.06, 152.80 (3 carbon signals missing/overlapping); MS-ESI for
12 $[C_{72}H_{116}N_2O_6-H]^+$ calculated (found): 1105.8912 (1105.8862); Elemental Analysis
13 (%) for $[C_{72}H_{116}N_2O_6]$ calculated (found): C, 78.21 (78.20); H, 10.57 (10.54); N, 2.53
14 (2.75).

15 ***A(10)Q(6,10/6,10)*** 1,2-Didecyloxy-4,5-dinitrobenzene: 0.4378 g, 0.911 mmol; 3,6-
16 didecyloxy-2,7-dihexyloxy-phenanthrene-9,10-dione: 0.110 g, 0.153 mmol; Final
17 product: 0.0805 g, 0.0728 mmol, 48 %; 1H NMR ($CDCl_3$, 400 MHz) δ 0.87-0.90 (m, 12
18 H), 0.95 (t, 6H, J = 7.0 Hz), 1.29-1.48 (m, 58 H), 1.53-1.65 (m, 12 H), 1.93-2.03 (m, 12
19 H), 4.27 (t, 8H, J = 6.4 Hz), 4.35 (t, 4 H, J = 6.6 Hz), 7.52 (s, 2 H), 7.76 (s, 2H), 8.76 (s, 2
20 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.07, 14.10, 22.67, 22.69, 25.85, 26.10, 26.17,
21 28.97, 29.31, 29.36, 29.37, 29.42, 29.44, 29.54, 29.59, 29.61, 29.64, 29.68, 31.67,
22 31.92, 69.08, 69.12, 69.13, 69.69, 106.57, 106.78, 106.80, 108.06, 124.25, 125.70,
23 139.14, 139.48, 149.37, 151.01, 152.77 (23 carbon signals missing/overlapping);

1 MS-ES for $[C_{72}H_{116}N_2O_6-H]^+$ calculated (found): 1105.8912 (1105.8997); elemental
2 analysis (%) for $[C_{72}H_{116}N_2O_6]$ calculated (found): C, 78.21 (78.26); H, 10.57 (10.55);
3 N, 2.53 (2.80)
4

5 Results

6 The three quinones **Q(6,10|6,10)**, **Q(6,10|10,6)** and **Q(10,6|10,6)** were prepared
7 as previously reported, using a regiospecific synthesis developed in our laboratory
8 to access the dicyanobenzoquinoxalines described above (Scheme 2).³³ Briefly, this
9 pathway hinges on the regioselective preparation of diphenylacetylenes, which can
10 then be efficiently converted to the corresponding benzil by DMSO/I₂ oxidation.
11 These diketones were then readily cyclized to the appropriate quinone in the
12 presence of VOF₃ and boron trifluoride etherate.
13

14 INSERT SCHEME 2 HERE

15 **Scheme 2.** Synthetic route for the synthesis of quinones **Q(w,x|y,z)**.
16

17 The diamines **A(m)** were prepared according to reported procedures.¹⁴ Because
18 these electron-rich compounds tend to be unstable towards oxidation, they were
19 isolated as their acid chlorides, which were used directly in the condensation with
20 the quinones using the conditions employed for the production of
21 **A(m)Q(6,6|10,10)**.

22 The liquid crystal properties of the resulting dibenzophenazines were investigated
23 by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and

variable temperature x-ray diffraction (VT-XRD). Upon heating, all compounds exhibit two peaks in the DSC endotherm. The low temperature transition has a large enthalpy and is assigned as the melting from a crystalline solid to a liquid crystal phase. The second, higher temperature, transition, has a much lower enthalpy and is consistent with the clearing of the liquid crystal to an isotropic phase.

POM studies confirmed that each sample transforms from a birefringent fluid into an optically isotropic liquid at its higher temperature transition, confirming its identification as the clearing transition. Slow cooling of these compounds from their isotropic phases affords either dendritic (Figure 1) or pseudo focal conic (Figure 2) textures characteristic of columnar hexagonal (Col_h) liquid crystal phases. These materials are highly fluid in the vicinity of the clearing temperature, but rapidly become more viscous as the temperature decreases; this behavior is typical of columnar phases.

The observed POM textures are generally comprised of bright (*i.e.* birefringent) domains interspersed with extensive dark regions. The latter areas correspond to domains in which the columns are homeotropically aligned. Mechanical deformation of these samples, accomplished by gently pressing on the coverslip with a spatula tip, causes the dark domains to become birefringent (Figure 3).

The formation of Col_h phases was confirmed by VT-XRD. The LC phase of each compound shows two peaks at low angles that index to the (100) and (110) peaks of a hexagonal lattice, as well as two relatively broad peaks at wider angles, which were assigned to the alkyl halo and π - π stacking distance (Table 1). Within each series, the intercolumnar spacing, a , shows very little variation. As expected, this

spacing increases slightly upon going from *series 1* ($m=6$) to *series 2* ($m=8$) to *series 3* ($m=10$).

INSERT FIGURE 1 HERE

Figure 1. Polarized optical micrographs of dendritic textures of Col_h phase of (a) $\text{A}(10)\text{Q}(6,10|6,10)$ at 110°C , (b) the same field of view, imaged using a 530 nm quarter wave plate, and (c) $\text{A}(8)\text{Q}(6,10|10,6)$ at 115°C .

INSERT FIGURE 2 HERE

Figure 2. Polarized optical micrographs of the pseudo focal conic fan textures of the Col_h phase of (a) $\text{A}(10)\text{Q}(6,10|10,6)$ at 130°C , and (b) $\text{A}(6)\text{Q}(6,10|10,6)$ at 125°C .

INSERT FIGURE 3 HERE

Figure 3. Polarized optical micrographs of $\text{A}(8)\text{Q}(6,10|10,6)$ at 130°C (a) before and (b) after shearing. Note that the dark central domain in (a) becomes birefringent after deformation.

INSERT TABLE 1 HERE

Table 4. X-ray diffraction data for Col_h phases of $\text{A}(n)\text{Q}(w,x|y,z)$

Discussion

The phase properties of all new compounds are summarized in Tables 2-4, along with those of the previously reported derivatives $\text{A}(m)\text{Q}(6,6|10,10)$. The compounds are divided into three series, corresponding to different values of m (6,

8 and 10). Each series is comprised of five isomers; four of the isomers have identical sets of groups (two C₆ and two C₁₀ chains) on the phenanthrene portion of the molecule, and differ only in the disposition of these moieties. Two of the isomers in each series [A(m)Q(6,10|10,6) and A(m)Q(10,6|6,10)] have higher symmetry than the remaining two, [A(m)Q(6,10|6,10) and A(m)Q(6,6|10,10)], allowing us to assess the impact of symmetry in these systems.

INSERT TABLE 2 HERE

Table 2. Phase behavior of *series 1*, A(m)Q(w,x|y,z), m = 6

INSERT TABLE 3 HERE

Table 3. Phase behavior of *series 2*, A(m)Q(w,x|y,z), m = 8

INSERT TABLE 4 HERE

Table 4. Phase behavior of *series 3*, A(m)Q(w,x|y,z), m = 10

In the analyses that follow, we will treat the trends in the melting and clearing transitions separately. Although there is a tendency in the literature to conflate the liquid crystal phase range with its stability, it is important to note that mesophase breadth arises from two distinct and largely independent equilibria. Whereas the upper limit of the LC phase results from the balance between the mesophase and the isotropic liquid, the lower bound is determined by the stability of not only the liquid

crystal, but also the crystalline solid. Because we expect appreciable differences in the crystalline solids across a series, the melting and clearing transitions are anticipated to be largely independent of one another. Indeed, we find that there is no correlation between the clearing and melting temperatures (Figure 4) across the series being examined in the current work.

INSERT FIGURE 4 HERE

Figure 4. Plot of melting points (T_m) versus clearing temperatures (T_c): *series 1* (circles), *series 2* (squares) and *series 3* (triangles).

The phase transitions of the compounds are shown graphically in Figure 5. Notably, the melting temperatures within each series show considerable variation. For example, in *series 1* ($m=6$) there is a 29° C change between the lowest melting derivative **A(6)Q(6,6|10,10)** and the isomer that melts at the most elevated temperature, **A(6)Q(10,6|6,10)**. Similar ranges of melting points are observed for *series 2* ($\Delta T_m=28^\circ\text{C}$) and *series 3* ($\Delta T_m=33^\circ\text{C}$). Variations in clearing temperature were generally much smaller (between 8-16°C), suggesting that this transition is less sensitive to structural perturbations than the melting point, consistent with earlier findings from our lab.³²

INSERT FIGURE 5 HERE

Figure 5. Graphical representation of the phase ranges of mesogens discussed in this work. Cr=crystalline solid (black), Col_h=columnar hexagonal liquid crystal (blue), I=isotropic liquid (grey).

In an effort to determine whether these variations follow a pattern, we compared the melting (T_m) temperatures within each of *Series 1-3* (Figures 6). While, there appear to be few generalizations that can be made from this plot, it is notable that compounds **A(m)Q(6,6|10,10)** consistently melt at significantly lower temperatures than their isomers. Indeed, in only one case, (**A(6)Q(6,10|6,10)**), does another compound possess a lower transition; in all other instances, the melting points of **A(m)Q(6,6|10,10)** are depressed 17-30°C relative to other members of the series. This observation is consistent with earlier observations that derivatives of **Q(6,6|10,10)** exhibit anomalously unstable crystalline phases.

INSERT FIGURE 6 HERE

Figure 6. Plot of melting temperatures (T_m) for compounds **A(m)Q(w,x|y,z)**; $m=6$ (*series 1*, blue circles), $m=8$ (*series 2*, black squares), $m=10$ (*series 3*, red triangles).

INSERT FIGURE 7 HERE

Figure 7. Plot of clearing temperatures (T_c) for compounds **A(m)Q(w,x|y,z)**; $m=6$ (*series 1*, blue circles), $m=8$ (*series 2*, black squares), $m=10$ (*series 3*, red triangles).

It is tempting to ascribe the pronounced lowering of the melting points of **A(m)Q(6,6|10,10)** to symmetry effects. Over a century ago, Thomas Carnelley made the observation that symmetrical molecules tend to have higher melting points than their lower symmetry isomers.^{34,35} This rule has subsequently been found to be broadly applicable, and molecular symmetry is an important predictor of the

1 melting point of solids to isotropic liquids.³⁶⁻⁴⁴ We have shown that Carnelley's rule,
2 which remains largely a phenomenological description of the melting of solids to
3 isotropic liquids, also generally holds for transitions between solids and liquid
4 crystals.³²⁻³³ Compounds **A(m)Q(6,6|10,10)** fit with this overall trend; these
5 molecules are less symmetric than **A(m)Q(6,10|10,6)** and **A(m)Q(10,6|6,10)**, and
6 melt at lower temperatures.

7 However, Carnelley's rule (as it applies to crystal-to-liquid crystal transitions)
8 appears to break down for compounds **A(m)Q(6,10|6,10)**. These molecules have
9 the same symmetry as **A(m)Q(6,6|10,10)**, yet their melting points are generally
10 much higher, and are, overall, similar to or even higher than those of their more
11 symmetric analogs. This observation suggests that symmetry is not the primary
12 factor governing the melting transitions of these compounds. Competing effects,
13 such as molecular shape, may either mitigate the impact of symmetry for
14 **A(m)Q(6,10|6,10)**, or give rise to apparent symmetry effects that are merely
15 coincidental in the cases of **A(m)Q(6,6|10,10)**. At the present time, it is difficult to
16 separate these effects.

17 Few regularities are apparent when comparing the trends in clearing temperatures
18 (Figure 7). Lower symmetry derivatives **A(m)Q(6,6|10,10)** and **A(m)Q(6,10|6,10)**
19 do not show any substantial depression in their clearing points relative to
20 symmetric isomers, consistent with our finding that these transitions are insensitive
21 to molecular symmetry.^{16,32,33}

22 One generalization that can be made with respect to clearing temperatures is that
23 the **A(m)Q(6,10|10,6)** isomers consistently clear at substantially lower

temperatures than corresponding **A(m)Q(10,6|6,10)** derivatives. This regularity likely originates from differences in molecular shape, and specifically the molecular ellipticity. Columnar phases typically arise from disc-shaped mesogens because deviations from circularity tend to hinder the ability of molecules to pack in hexagonal lattices, leading to a destabilization of the mesophase. This could explain why the roughly circular compound **A(10)Q(10,6|6,10)** has a clearing temperature that is 16° C higher than that of its much more elliptical isomer **A(10)Q(6,10|10,6)** (Figure 8).

INSERT FIGURE 8 HERE

Figure 8. Space filling models of (a) **A(10)Q(6,10|10,6)** and (b) **A(10)Q(10,6|6,10)**. The models are inscribed in circles to highlight deviations of molecular from circularity.

Conclusion

In the present work, we report the synthesis of nine new compounds, which, in conjunction with three previously prepared analogs, allow the relationships between molecular structure and liquid crystal properties to be explored. It was found that phase behavior within each of three series of isomers strongly depends on the position of the flexible side chains, with the melting points being particularly sensitive to these changes. While the underlying causes of these perturbations require further exploration, our results suggest that the importance of molecular symmetry are less important than previously believed. Ongoing efforts in our lab

are targeted towards further elucidating the potentially competing effects of molecular symmetry and shape.

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Figure 1. Polarized optical micrographs of dendritic textures of Colh phase of (a) $A(10)Q(6,10|6,10)$ at 110°C , (b) the same field of view, imaged using a 530 nm quarter wave plate, and (c) $A(8)Q(6,10|10,6)$ at 115°C .

143x58mm (150 x 150 DPI)

Figure 2. Polarized optical micrographs of the pseudo focal conic fan textures of the Colh phase of (a) A(10)Q(6,10|10,6) at 130° C, and (b) A(6)Q(6,10|10,6) at 125° C.

115x47mm (150 x 150 DPI)

Draft

Figure 3. Polarized optical micrographs of A(8)Q(6,10 |10,6) at 130° C (a) before and (b) after shearing. Note that the dark central domain in (a) becomes birefringent after deformation.

103x45mm (150 x 150 DPI)

Figure 5. Graphical representation of the phase ranges of mesogens discussed in this work. Cr=crystalline solid (black), Col_h=columnar hexagonal liquid crystal (blue), I=isotropic liquid (grey).

174x172mm (150 x 150 DPI)

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Compound	Temp (°C)	d-spacing (Å)	Miller indices (hkl)	Lattice constant
A(6)Q(6,10 6,10)	100	20.7	100	a = 23.9 Å
		11.9	110	
		4.3	alkyl halo	
		3.6	π - π	
A(6)Q(6,10 10,6)	110	20.7	100	a = 23.9 Å
		11.9	110	
		4.2	alkyl halo	
		3.6	π - π	
A(6)Q(10,6 6,10)	110	20.9	100	a = 24.2 Å
		12.1	110	
		4.2	alkyl halo	
		3.6	π - π	
A(8)Q(6,10 6,10)	105	21.4	100	a = 24.7 Å
		12.3	110	
		4.2	alkyl halo	
		3.6	π - π	
A(8)Q(6,10 10,6)	100	21.2	100	a = 24.5 Å
		12.3	110	
		4.3	alkyl halo	
		3.6	π - π	
A(8)Q(10,6 6,10)	115	21.6	100	a = 24.9 Å
		12.5	110	
		4.3	alkyl halo	
		3.6	π - π	
A(10)Q(6,10 6,10)	100	22.2	100	a = 25.7 Å
		12.9	110	
		4.3	alkyl halo	
		3.5	π - π	
A(10)Q(6,10 10,6)	90	21.9	100	a = 25.3 Å
		12.7	110	
		4.3	alkyl halo	
		3.6	π - π	
A(10)Q(10,6 6,10)	105	22.2	100	a = 25.7 Å
		12.8	110	
		4.3	alkyl halo	
		3.6	π - π	

Compound	Phase ^a	$T_t / ^\circ\text{C}$ ($\Delta H / \text{J g}^{-1}$) ^b	Phase	$T_t / ^\circ\text{C}$ ($\Delta H / \text{J g}^{-1}$)	Phase
A(6)Q(10,6 6,10)	Cr	$\xrightarrow{69.9 (61.9)}$ $\xleftarrow{15.8 (-28.0)}$	Col _h	$\xrightarrow{137.2 (3.8)}$ $\xleftarrow{134.1 (-3.5)}$	I
A(6)Q(6,10 10,6)	Cr	$\xrightarrow{60.1 (28.8)}$ $\xleftarrow{24.7 (-48.5)}$	Col _h	$\xrightarrow{130.6 (3.8)}$ $\xleftarrow{128.5 (-4.0)}$	I
A(6)Q(6,10 6,10)	Cr	$\xrightarrow{40.7 (50.4)}$ $\xleftarrow{20.6 (-5.5)}$	Col _h	$\xrightarrow{134.4 (4.2)}$ $\xleftarrow{132.1 (-4.4)}$	I
A(6)Q(6,6 10,10) ^c	Cr	$\xrightarrow{43.2 (42.3)}$ $\xleftarrow{12.2 (-4.0)}$	Col _h	$\xrightarrow{129.5 (3.5)}$ $\xleftarrow{126.6 (-3.3)}$	I

^a transition temperatures and enthalpies determined by DSC at a scan rate= 5 C°/min; ^b Cr=crystal, Col_h=columnar hexagonal, I = isotropic; ^c ref [33]

115x51mm (150 x 150 DPI)

Draft

Compound	Phase ^a	$T_t / ^\circ\text{C}$ ($\Delta H / \text{J g}^{-1}$) ^b	Phase	$T_t / ^\circ\text{C}$ ($\Delta H / \text{J g}^{-1}$)	Phase
A(8)Q(10,6 6,10)	Cr	$\begin{matrix} \xrightarrow{70.8 (70.6)} \\ \xleftarrow{41.0 (-63.5)} \end{matrix}$	Col _h	$\begin{matrix} \xrightarrow{133.6 (4.3)} \\ \xleftarrow{130.9 (-4.5)} \end{matrix}$	I
A(8)Q(6,10 10,6)	Cr	$\begin{matrix} \xrightarrow{65.7 (64.8)} \\ \xleftarrow{10.3 (-38.5)} \end{matrix}$	Col _h	$\begin{matrix} \xrightarrow{122.4 (3.3)} \\ \xleftarrow{119.5 (-2.7)} \end{matrix}$	I
A(8)Q(6,10 6,10)	Cr	$\begin{matrix} \xrightarrow{64.8 (32.5)} \\ \xleftarrow{16.3 (-5.5)} \end{matrix}$	Col _h	$\begin{matrix} \xrightarrow{123.0 (0.5)} \\ \xleftarrow{117.3 (-2.3)} \end{matrix}$	I
A(8)Q(6,6 10,10) ^a	Cr	$\begin{matrix} \xrightarrow{43.4 (35.7)} \\ \xleftarrow{15.8 (-3.7)} \end{matrix}$	Col _h	$\begin{matrix} \xrightarrow{128.3 (0.5)} \\ \xleftarrow{126.0 (-1.9)} \end{matrix}$	I

^a transition temperatures and enthalpies determined by DSC at a scan rate= 5 C°/min; ^b Cr=crystal, Col_h=columnar hexagonal, I = isotropic; ^c ref [33]

116x52mm (150 x 150 DPI)

Draft

Compound	Phase ^a	$T_t / ^\circ\text{C} (\Delta H/\text{J g}^{-1})^b$	Phase	$T_t / ^\circ\text{C} (\Delta H/\text{J g}^{-1})$	Phase
A(10)Q(10,6 6,10)	Cr	$\xrightarrow{58.2 (31.5)}$ $\xleftarrow{18.8 (-48.9)}$	Col _h	$\xrightarrow{121.0 (3.7)}$ $\xleftarrow{118.2 (-3.6)}$	I
A(10)Q(6,10 10,6)	Cr	$\xrightarrow{70.6 (66.7)}$ $\xleftarrow{8.9 (-44.6)}$	Col _h	$\xrightarrow{105.1 (1.7)}$ $\xleftarrow{102.2 (-2.4)}$	I
A(10)Q(6,10 6,10)	Cr	$\xrightarrow{74.4 (70.8)}$ $\xleftarrow{13.6 (-48.8)}$	Col _h	$\xrightarrow{116.9 (1.9)}$ $\xleftarrow{107.0 (-3.0)}$	I
A(10)Q(6,6 10,10) ^a	Cr	$\xrightarrow{40.9 (37.5)}$ $\xleftarrow{16.3 (-28.1)}$	Col _h	$\xrightarrow{108.4 (1.61)}$ $\xleftarrow{104.6 (-1.9)}$	I

^a transition temperatures and enthalpies determined by DSC at a scan rate= 5 C°/min; ^b Cr=crystal, Col_h=columnar hexagonal, I = isotropic; ^c ref [33]

115x52mm (150 x 150 DPI)

CN-Q(6,6|10,10) $R^1 = R^2 = C_6H_{13}$; $R^3 = R^4 = C_{10}H_{21}$

CN-Q(6,10|6,10) $R^1 = R^3 = C_6H_{13}$; $R^2 = R^4 = C_{10}H_{21}$

CN-Q(6,10|10,6) $R^1 = R^4 = C_6H_{13}$; $R^2 = R^3 = C_{10}H_{21}$

CN-Q(10,6|6,10) $R^2 = R^3 = C_6H_{13}$; $R^1 = R^4 = C_{10}H_{21}$

29x8mm (600 x 600 DPI)

Draft