Thermotropic uniaxial and biaxial nematic, and smectic phases in bent-core mesogens.

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Supporting Information

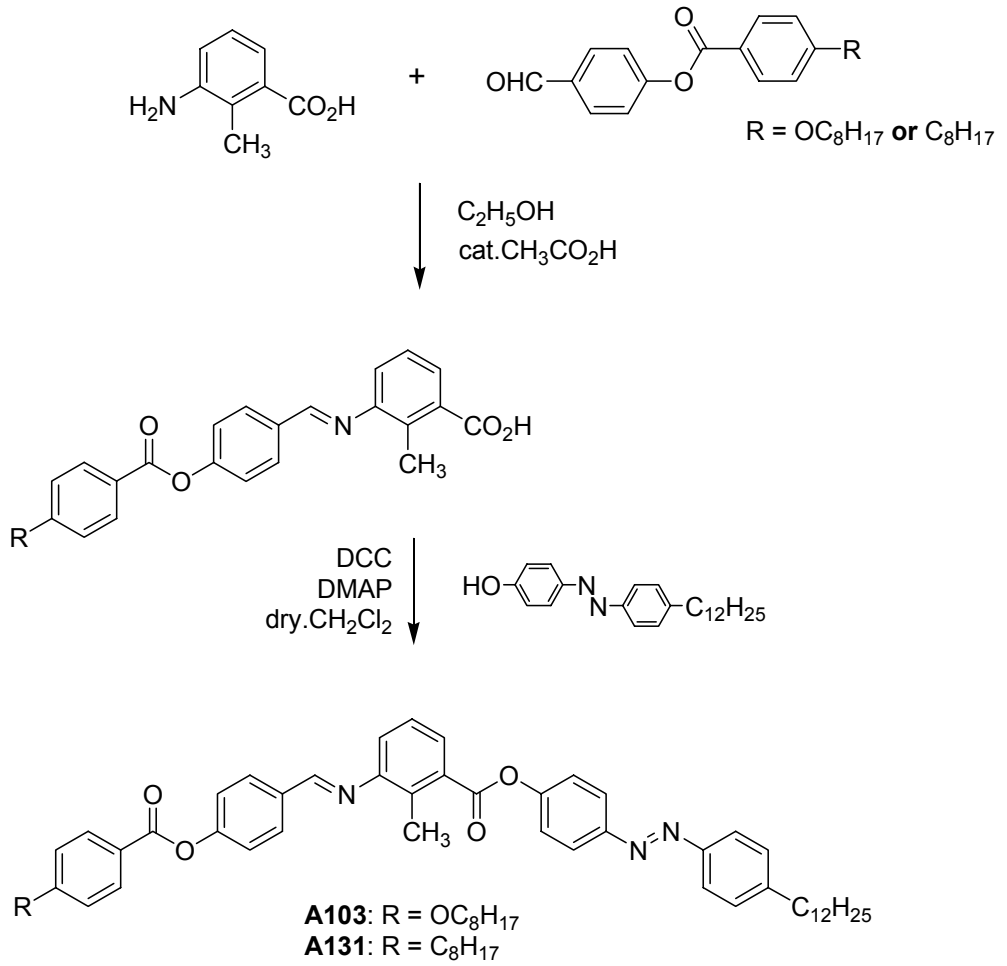
1. Synthesis and characterization

The synthesis of compounds 4-((4-dodecylphenyl)diazenyl)phenyl 2-methyl-3-(4-(4-(octyloxy)benzoyloxy)benzyledeneamino)benzoate, (***A103***) and 4-((4-dodecylphenyl)diazenyl) phenyl 2-methyl-3-(4-(4-octylbenzoyloxy)benzyledeneamino)benzoate, (***A131***) was achieved using a procedure, shown in scheme 1, similar to the one previously reported[15,16] by us. In the present case, 2-methyl-3-nitrobenzoic acid was reduced to the corresponding amine by catalytic hydrogenation. This amine formed the central core, to which two different types of segments were attached on either side at 1 and 3 positions to obtain the highly unsymmetric bent-core compounds ***A103*** and ***A131***.

The general procedure followed to obtain *A103* and *A131* is as follows:

3-Amino-2-methylbenzoic acid (1.0 mmol) and 4-formylphenyl 4-(octyloxy/octyl) benzoate (1.0 mmol) were dissolved in ethyl alcohol (40 ml). To this was added 2-3 drops of glacial acetic acid and the reaction mixture was refluxed for 6 hours. The solid product, 2-methyl-3-(4-(4-(ctyloxy/octyl)benzoyloxy)benzylideneamino)benzoic acid formed, was filtered and

purified by several repeated recrystallizations. The pure acid thus obtained (1.0 mmol), 4-((-dodecylphenyl)diazenyl)phenol (1.0 mmol), 1,3-dicyclohexylcarbodiimide (1.1 mmol) and



Scheme 1

dimethylaminopyridine (20 mg) were dissolved in dry dichloromethane (40 ml). The reaction mixture was stirred at room temperature for 12 hours. Filtered the dicyclohexyl urea formed and distilled the dichloromethane from the filtrate to obtain crude A103/A131. This was repeatedly recrystallized several times using acetone to obtain the final products A103/A131, in the purest form. The spectral data and CHN analysis obtained for the two compounds are given below:

A103: ^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.38 (s, 1H, -CH=N-), 6.94 – 8.2 (m, 19H, ArH), 4.08 (t, 2H, Ar-OCH_2), 2.7 (m, 5H, Ar-CH_3 and Ar-CH_2), 1.2 – 1.9 (m, 32H, -CH_2), 0.89 (m, 6H, -CH_3). Elemental anal.: calcd. for $C_{54}H_{65}N_3O_5$, C, 77.57, H, 7.84, N, 5.03; found, C, 77.78, H, 7.69, N, 4.92%.

A131: ^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.40 (s, 1H, -CH=N-), 7.12 - 8.19 (m, 19H, ArH), 2.62 - 2.80 (m, 7H, Ar-CH_3, Ar-CH_2), 1.19 – 1.80 (m, 32H, -CH2), 0.91 (m, 6H, -CH_3). Elemental anal.: cald. for $C_{54}H_{65}N_3O_4$, C, 79.08, H, 7.99, N, 5.12; found: C, 79.24, H, 8.19, N, 4.98 %.

2. Polarizing optical textures

For the electro-optical studies, the sample was sealed in flat glass cells of ~ 10 *μm* thickness. Glass plates with transparent but electrically conducting indium-tin-oxide (ITO) layer and polyimide alignment layers with homeotropic anchoring were assembled using 10 *μm* spacers. The microscopic textural observations were carried out using a Mettler FP82HT hot stage in conjunction with Olympus BX60F-3 polarizing optical microscope. The transition temperatures of different phase transitions and the associated enthalpies were determined from differential scanning calorimetric scans (DSC7, Perkin-Elmer). The heating and cooling rates were 5°C/min.

3. Synchrotron x-ray diffraction studies

For structural characterization, the samples were sealed in 1.5 *mm* diameter Lindeman capillaries with 10 μm thick walls. The samples were taken above the clearing point and cooled in the presence of a magnetic field of ~2.5 kG from the isotropic phase to the first liquid crystalline phase. Sample temperature was controllable with a precision of ±0.1°C using a home made oven and temperature controller. The 2θ-scans were generated from the 2-D diffraction

patterns using the software package FIT2D developed by A. P. Hammersley of European Synchrotron Radiation Facility.

X-ray work was performed at the Midwestern Universities Collaborative Team's sector at the Advanced Photon Source. Diffraction patterns were acquired using a high-resolution image plate detector Mar-3450 (MAR Research) placed at a distance of 1158.9 *mm* from the sample. The wavelength of x rays was 0.7653 Å.