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A "Peelable Banana-shaped" Mesogen: A First Low Molar Mass Monodispersive Bent-Rod Dimer Exhibiting the Biaxial Nematic and Smectic A Phases**

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General

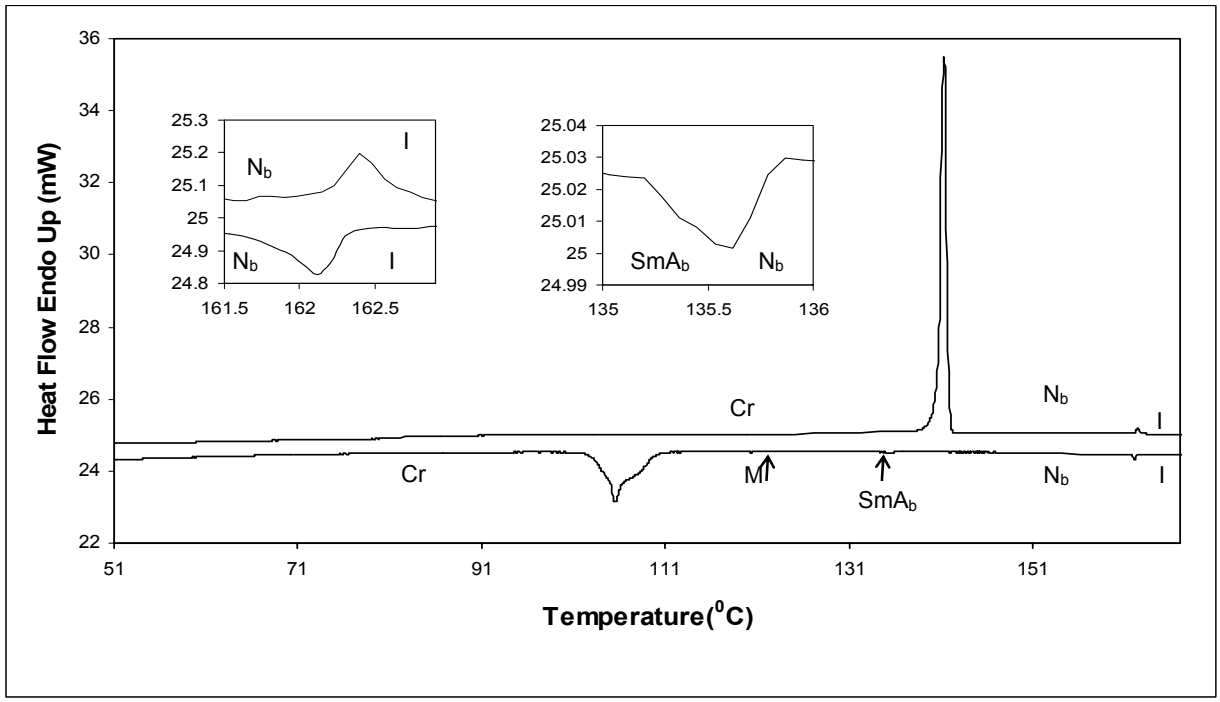
Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselge 60, F_{254}). IR spectra were recorded using a Perkin-Elmer 1000 FTIR spectrometer. ^{1}H NMR & ^{13}C NMR spectra were recorded using a Bruker AMX-400 (400 MHz) or Bruker Aveance series DPX-200 (200 MHz) spectrometers. For ^{1}H NMR spectra, the chemical shifts are reported in ppm relative to tetramethylsilane as an internal standard. Mass spectra were recorded on a Jeol-JMS-600H spectromter in FAB^{+} mode using 3-nitrobenzylalcohol as a liquid matrix. Elemental analyses were carried out using a Eurovector EA 3000 series CHNOS analyzer. The compounds were investigated for liquid crystalline behaviour using a polarizing optical microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90), and by differential scanning calorimetry (Perkin Elmer DSC7). X-ray diffraction studies were carried out using an Image Plate Detector (MAC Science, Japan) equipped with double mirror focusing optics, with the sample contained in a Lindemann capillary tube.

Molecular structural characterization data for bent-rod dimers

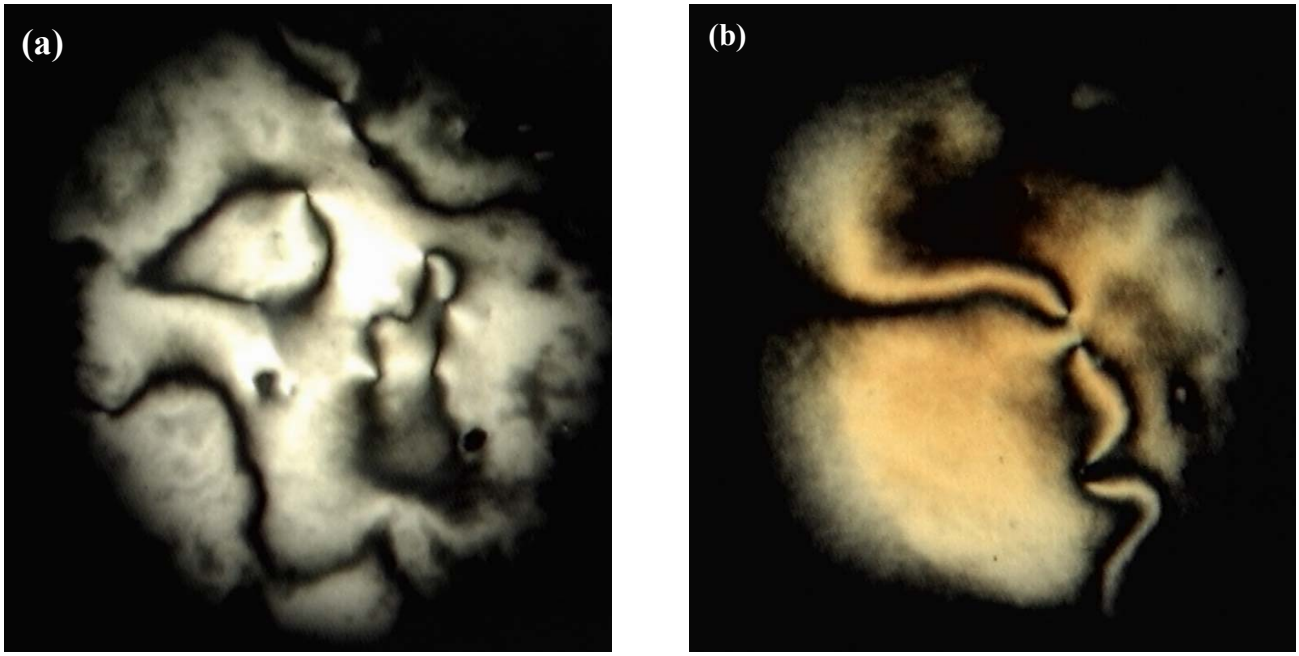
1a: A yellow solid; IR (KBr Pellet): ν_{max} in cm^{-1} 2921, 2852, 2223, 1731, 1603 and 1511; ^{1}H NMR (400MHz, $CDCl_3$): δ 13.32 (s, 1H, 1 × -OH), 8.66 (s, 1H, 1 × -CH=N), 8.29 (d, *J* = 8.6Hz, 2H, Ar), 8.15 (t, *J* = 7.9, 4H, Ar), 7.66 (AA'BB' quartet, 4H, Δν=18.46, *J*=8.32, 4H, Ar), 7.54-7.37 (m, 6H, Ar), 7.22-7.16 (m, 3H, Ar), 7.00-6.97 (m, 6H, Ar), 6.90 (d, *J* = 1.72, 1H, Ar), 6.84 (dd, *J* = 1.98, 8.4, 1H, Ar), 4.11-4.04 (m, 6H, 3 × -OCH_2-), 1.94-1.71 (m, 6H, 3 × -CH_2-), 1.54-1.28 (m, 16H, 8× -CH_2-), and

0.89 (t, J = 6.4, 3H, 1 × -CH_3); ^{13}C (100MHz, $CDCl_3$): δ 164.38, 164.33, 164.27, 163.93, 163.62, 162.68, 159.75, 155.61, 155.20, 151.81, 149.70, 145.28, 133.43, 132,60,132.45, 131.88,131.51,130.27, 128.39, 127.12, 126.71, 122.19, 121.47, 121.02, 120.14, 119.16, 119.09, 117.02, 115.17, 114.51, 114.43, 113.24, 110.69, 110.20, 68.47, 68.13, 67.93, 31.92, 29.58, 29.39, 29.34, 29.13, 29.00, 28.89, 26.02, 22.77, 22.70 and 14.12; FAB mass: 993.3 $[M]^+$ calcd for $C_{62}H_{60}O_{10}N_2$; Elemental analysis: Calcd (Found): C 74.98 (74.91); H 6.08 (5.90); N 2.82 (2.87)

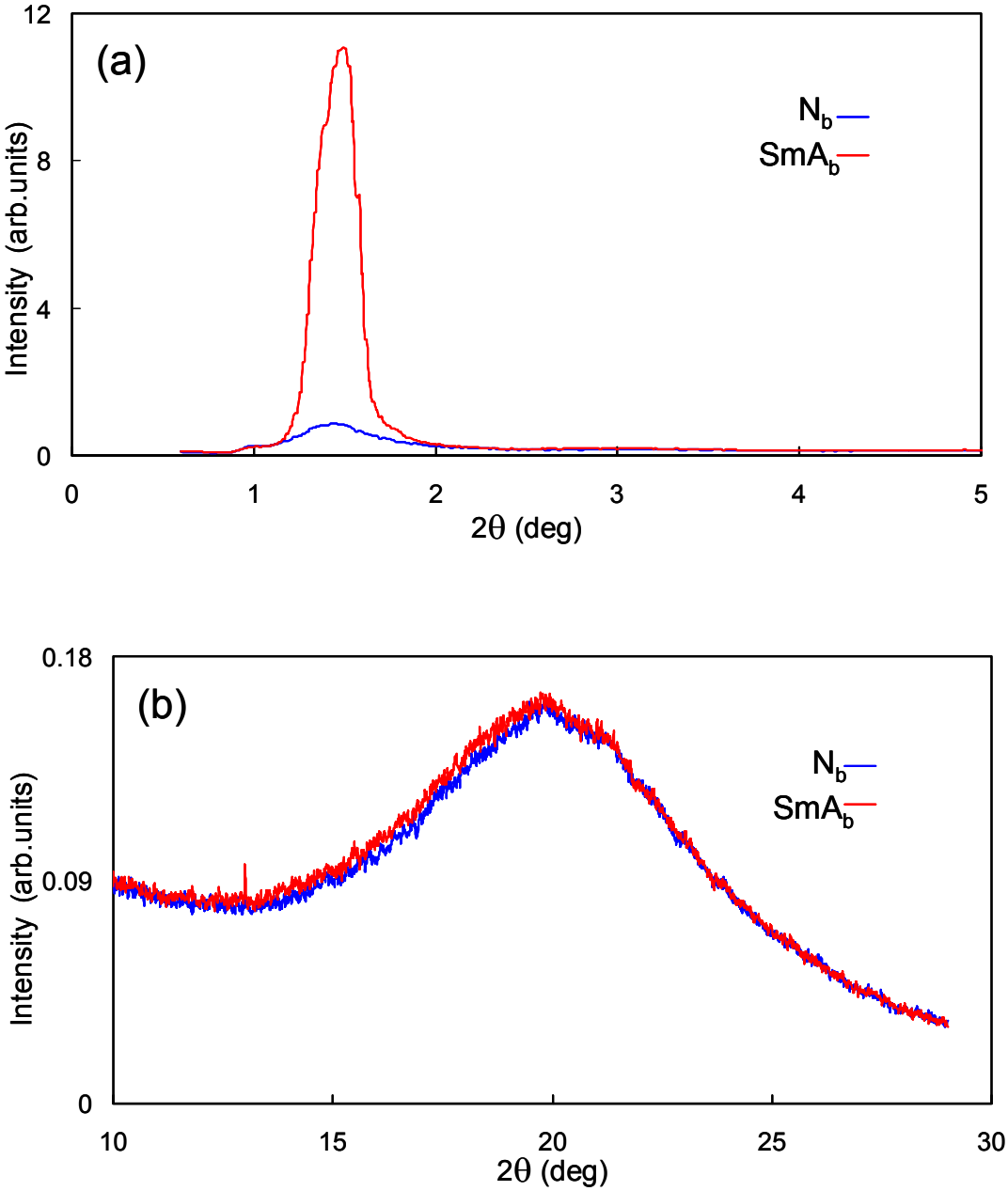
1b: An yellow solid; IR (KBr Pellet): ν_{max} in cm^{-1} 2923, 2853, 2222, 1731, 1603 and 1578; ^{1}H NMR (400MHz, $CDCl_3$): δ 13.35 (s, 1H, 1 × -OH), 8.65 (s, 1H, 1 × -CH=N), 8.29 (d, J = 8.7Hz, 2H, Ar), 8.14 (t, J = 8.7, 4H, Ar), 7.65 (AA'BB' quartet, 4H, Δν=17.7, J=9.3, 4H, Ar), 7.51-7.37 (m, 6H, Ar), 7.21-7.16 (m, 3H, Ar), 7.00-6.96 (m, 6H, Ar), 6.90 (d, J = 2.08, 1H, Ar), 6.84 (dd, J = 2.16, 8.4, 1H, Ar), 4.09-4.02 (m, 6H, 3 × -OCH_2), 1.87-1.79 (m, 6H, 3 × -CH_2), 1.59-1.28 (m, 18H, 6× -CH_2-), and 0.89 (t, J = 6.7, 3H, 1 × -CH_3); ^{13}C (100MHz, $CDCl_3$): δ 164.35, 164.30, 164.25, 163.93, 163.94, 162.69, 159.82, 155.63, 155.24, 151.84, 149.73, 145.30, 133.39, 132,58, 132.44, 131.85, 131.47, 130.24, 128.36, 127.11, 126.73, 122.17, 121.46, 121.07, 120.11, 119.13, 119.05, 117.05, 115.18, 114.52, 114.43, 113.22, 110.68, 110.22, 68.48, 68.21, 68.03, 31.91, 29.56, 29.37, 29.32, 29.19, 29.13, 29.07, 29.01, 25.84, 22.68 and 14.08; FAB mass: 1007.8 $[M]^{+1}$ calcd for $C_{63}H_{62}O_{10}N_2$; Elemental analysis: Calcd. (Found): C 75.13 (75.25); H 6.20 (6.07); N 2.78 (3.22)



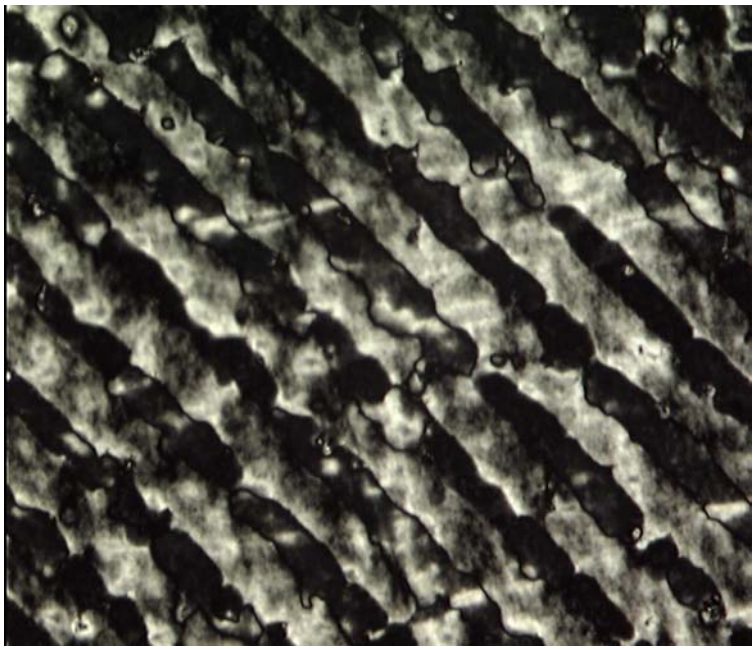
Differential scanning calorimetric thermograms obtained in the heating (upper profile) and cooling (lower profile) modes for the bent-rod dimer **1b** at a rate of 5 ^{o}C / min. The regions in the vicinity of the I-N_b and N_b-SmA_b transitions are shown as insets.



Texture observed in a free-standing film in (a) SmA_b and (b) N_b phases.
Notice the exclusive presence of 2-brush disclinations



"1d-cut" of the Xray diffraction pattern in the SmA_b and N_b phases in the (a) low-angle and (b) wide-angle regions.



Photomicrograph of the alternate dark and bright stripe pattern seen in the SmA_b phase. The width of the stripe is ~ 50 μm.