Sensitivity of the N_{TB} Phase Formation to the Molecular Structure of Imino-linked Dimers

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XRD data:

Table S1. X-ray data from the 2D patterns: ($2\theta_{\text{obs}}$... experimental scattering angle; d_{obs} ... experimental d value; n ... order of reflection and d ... layer spacing: for the SmC_C phase).

a) Position of the maxima of the diffuse scattering and the layer reflections in the small angle region (because of the shape of the diffuse scattering curves the values are of limited accuracy, especially those for the very weak innermost maxima or shoulders):

Compound	$T/^{\circ}\text{C}$	Phase	$2\theta_{\text{obs}}/^{\circ}$	d_{obs}/nm	n	d / nm
NB_7-4	150	N	2.29	3.86		
			3.94	2.24		
	138	SmC _C	3.912	2.26	1	2.26
			7.813	1.13	2	
NB_9-4	150	N	3.74	2.36		
	130	N _x	3.69	2.40		
	126	SmC _C	3.740*	2.36*	1	2.36*
BN_7-4	145	N	2.29	3.85		
			4.01	2.20		
	132	N _x	2.32	3.80		
			3.99	2.21		
BN_9-6	160	N	3.58*	2.47*		
	125	SmC _C	3.509*	2.52*	1	2.52*
			6.999*	1.26*	2	
BS_7-6	100	N	2.39	3.70		
			4.24	2.08		
	91	N _x	2.42	3.64		
			4.26	2.08		
NS_7-4	150	N	2.47	3.58		
			4.16	2.12		
	120	N _x	2.48	3.57		
			4.20	2.10		
NS_7-6	140	N	2.32	3.82		
			3.98	2.22		
	120	N _x	2.32	3.80		
			4.04	2.19		
NS_7-8[#]	130	N	2.11	4.19		
			3.71	2.38		
	120	N _x	2.15	4.11		
			3.77	2.35		

* Data from wide angle patterns (sample – detector distance = 9.3 cm)

[#] The discrepancies between these values and those cited in [10] result from the very limited accuracy of the determination of the maxima for the inner diffuse scattering in the WAXD patterns used in [10].

b) Position of the maxima of the outer diffuse scattering:

Compound	$T/^{\circ}\text{C}$	Phase	$2\theta_{\text{obs}}/^{\circ}$	d_{obs}/nm
NB_7-4	160	N	19.5	0.46
	142	SmC _C	20.1	0.44
NB_9-4	144	N	19.5	0.46
	130	N _x	19.6	0.45
	126	SmC _C	19.6	0.45
BN_7-4	160	N	19.7	0.45
	136	N _x	19.9	0.45
BN_9-6	160	N	19.1	0.46
	125	SmC _C	19.6	0.45
BS_7-6	105	N	20.1	0.44
	92	N _x	20.3	0.44
NS_7-4	150	N	19.5	0.46
	120	N _x	19.9	0.45
NS_7-6	150	N	19.7	0.45
	120	N _x	20.2	0.44

Figure S1: 2D XRD patterns for samples of the NB_{7-n} series aligned in the magnetic field obtained on cooling from the isotropic liquid: SAXD for NB₉₋₄ at 150 °C (a) and 130 °C (b), WAXD for NB₇₋₄ at 160 °C (c) and at 142 °C (d), SAXD for NB₇₋₄ at 150 °C (e) and 138 °C (f) with corresponding SAX diffraction curves for NB₉₋₄ (g) and NB₇₋₄ (h) and (i) (inset: second-order layer reflection).

Figure S2: Azimuthal distribution of the outer and inner scattering (χ scans) in the 2D XRD patterns for a sample of **BN_9-6** at 160 and 125 °C aligned in the magnetic field obtained on cooling from the isotropic liquid. The outer scattering at 125 °C shows maxima at $\chi = 74, 253, 110,$ and 291° from which a tilt of the molecules with respect to the layer normal of about 18° can be calculated. The azimuthal distribution of the inner scattering at 160 °C at the upper meridian may be fitted by two Gauss curves showing maxima at $\chi = 156$ and 188° yielding a tilt angle of about 16° of the molecules in the smectic clusters.

Figure S3: 2D XRD patterns of the NS_{m-n} series for samples aligned in the magnetic field obtained on cooling from the isotropic liquid: SAXD for NS₇₋₈ at 160 °C (a), 130 °C (b) and at 120 °C (c), WAXD for NS₇₋₆ at 150 °C (d) and at 120 °C (e), SAXD for NS₇₋₆ at 140 °C (f) and at 120 °C (g), WAXD for NS₇₋₄ at 150 °C (h) and at 120 °C (i), SAXD for NS₇₋₄ at 150 °C (j) and at 120 °C (k).

Figure S4: 2D SAXD patterns for samples of BS₇₋₆ aligned in the magnetic field obtained on cooling from the isotropic liquid at 120 °C (a), at 100 °C (b), 91 °C (c).

Spectroscopic and analytical data for the new dimeric compounds

Spectroscopic data are given for one imine homologue of each series, since the only significant difference in the NMR spectra relates to the number of carbons in the alkoxy chains and alkylene spacer.

*N,N'-bis[6'-(4''-hexyloxybenzoyloxy)naphthalen-2'-ylmethylene]-heptane-1,7-diamine **BN_7-6**.*

¹H NMR (CDCl₃) δ: 0.94-0.96 (m, 6H), 1.36-1.41 (m, 8H), 1.45-1.54 (m, 10H), 1.76-1.81 (m, 4H), 1.83-1.87 (m, 4H), 3.69 (t, *J* = 6.7 Hz, 4H), 4.08 (t, *J* = 6.6 Hz, 4H), 7.01 (d, *J* = 8.9 Hz, 4H), 7.39 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.2 Hz, 2H), 7.70 (d, *J* = 2.0 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.94 (d, *J* = 8.9 Hz, 2H), 8.01 (dd, *J*₁ = 8.6 Hz, *J*₂ = 1.4 Hz, 2H), 8.06 (s, 2H), 8.14-8.20 (m, 4H), 8.44 (s, 2H) ppm. ¹³C NMR (CDCl₃) δ: 13.48, 22.06, 25.15, 26.81, 28.57, 28.73, 30.41, 31.04, 61.33, 67.87, 113.88, 118.31, 120.98, 121.49, 124.19, 127.64, 128.79, 129.48, 130.62, 131.83, 133.45, 134.65, 149.23, 160.05, 163.17, 164.44 ppm.

*N,N'-bis[4'-(6''-butyloxy-2''-naphthoyloxy)benzylidene]-heptane-1,7-diamine **NB_7-4**.*

¹H NMR (CDCl₃) δ: 1.02 (t, *J* = 7.4 Hz, 6H), 1.41 (s, 6H), 1.52–1.58 (m, 4H), 1.71–1.74 (m, 4H), 1.83–1.87 (m, 4H), 3.62 (t, *J* = 6.7 Hz, 4H), 4.11 (t, *J* = 6.5 Hz, 4H), 7.16 (d, *J* = 2.0 Hz, 2H), 7.21 (dd, *J*₁ = 8.9 Hz, *J*₂ = 2.4 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 4H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 4H), 7.86 (d, *J* = 9.0 Hz, 2H), 8.13 (dd, *J*₁ = 8.6 Hz, *J*₂ = 1.6 Hz, 2H), 8.29 (s, 2H), 8.68 (s, 2H) ppm. ¹³C NMR (CDCl₃) δ: 13.36, 18.80, 26.79, 28.72, 30.36, 30.71, 61.23, 67.41, 105.95, 119.66, 121.53, 123.63, 125.59, 126.52, 127.30, 128.71, 130.49, 131.29, 133.58, 137.17, 152.30, 158.99, 159.12, 164.71 ppm.

*N,N'-bis[4'-(6''-butyloxy-2-naphthoyloxy)-2'-hydroxybenzylidene]-heptane-1,7-diamine **NS_7-4***

¹H NMR (CDCl₃) δ: 1.05 (t, *J* = 7.4 Hz, 6H), 1.43-1.48 (m, 6H), 1.56–1.64 (m, 4H), 1.72–1.78 (m, 4H), 1.87–1.91 (m, 4H), 3.63 (t, *J* = 6.7 Hz, 4H), 4.15 (t, *J* = 6.5 Hz, 4H), 6.81 (dd, *J*₁ = 8.3 Hz, *J*₂ = 2.2 Hz, 2H), 6.89 (d, *J* = 2.2 Hz, 2H), 7.20 (d, *J* = 2.2 Hz, 2H), 7.25 (dd, *J*₁ = 8.9 Hz, *J*₂

= 2.5 Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.81 (d, $J = 8.7$ Hz, 2H), 7.90 (d, $J = 9.0$ Hz, 2H), 8.16 (dd, $J_1 = 8.6$ Hz, $J_2 = 1.9$ Hz, 2H), 8.36 (s, 2H), 8.70 (s, 2H), 14.08 (s, 2H) ppm. ^{13}C NMR (CDCl_3) δ : 13.85, 19.30, 27.03, 28.99, 30.70, 31.21, 58.96, 67.92, 106.48, 110.66, 121.17, 116.66, 120.13, 124.18, 126.12, 126.99, 127.80, 130.99, 131.79, 132.04, 137.66, 154.23, 159.43, 163.59, 163.87, 165.00 ppm.

N,N'-bis[4'-(4''-butoxybiphenoyloxy)benzylidene]-nonane-1,9-diamine **BPB_9-4**.

^1H NMR (CDCl_3) δ : 0.99 (t, $J=7.4$ Hz, 6H), 1.20-1.43 (m, 10H), 1.43-1.58 (m, 4H), 1.64-1.88 (m, 8H), 3.62 (t, $J=6.6$ Hz, 4H), 4.02 (t, $J=6.6$ Hz, 4H), 7.00 (d, $J=8.7$ Hz, 4H), 7.29 (d, $J=8.5$ Hz, 4H), 7.59 (d, $J=8.7$ Hz, 4H), 7.69 (d, $J=8.4$ Hz, 4H), 7.80 (d, $J=8.5$ Hz, 4H), 8.23 (d, $J=8.5$ Hz, 4H), 8.29 (s, 2H) ppm. ^{13}C -NMR (CDCl_3) δ : 13.32, 18.74, 26.81, 28.89, 28.98, 30.39, 30.81, 61.22, 67.37, 114.53, 121.45, 126.11, 126.83, 127.88, 128.69, 130.23, 131.46, 133.64, 145.61, 152.20, 159.04, 159.15, 164.35 ppm.

N,N'-Bis[4'-(4''-hexyloxybiphenoyloxy)-2'-hydroxybenzylidene]-nonane-1,9-diamine **BPS_9-6**.

^1H NMR (CDCl_3) δ : 0.92 (t, $J=6.6$ Hz, 6H), 1.20-1.59 (m, 22H), 1.60-1.75 (m, 4H), 1.75-1.93 (m, 4H), 3.58 (t, $J=6.4$ Hz, 4H), 4.00 (t, $J=6.5$ Hz, 4H), 6.74 (dd, $J_1=8.3$ Hz, $J_2=1.8$ Hz, 2H), 6.82 (d, $J=1.5$ Hz, 2H), 7.00 (d, $J=8.5$ Hz, 4H), 7.27 (d, $J=8.7$ Hz, 2H), 7.59 (d, $J=8.5$ Hz, 4H), 7.68 (d, $J=8.3$ Hz, 4H), 8.21 (d, $J=8.3$ Hz, 4H), 8.32 (s, 2H), 14.12 (s, 2H) ppm. ^{13}C -NMR (CDCl_3) δ : 13.99, 22.58, 25.71, 27.04, 29.15, 29.22, 29.32, 30.74, 31.58, 58.95, 68.20, 110.61, 112.04, 115.04, 116.68, 126.58, 127.38, 128.37, 130.74, 131.99, 146.08, 154.12, 159.64, 163.65, 163.77, 164.63 ppm.

Table S2. Analytical data for the new dimeric compounds comprising BN, NB and BPB mesogenic unit

Dimer	Analysis: Calc(Found)/%		
	C	H	N
BN_7-6 (C ₅₅ H ₆₂ N ₂ O ₆)	77.98(78.12)	7.38(7.41)	3.31(3.27)
BN_9-6 (C ₅₇ H ₆₆ N ₂ O ₆)	78.23(78.15)	7.60(7.48)	3.20(3.31)
BN_7-4 (C ₅₁ H ₅₄ N ₂ O ₆)	77.44(77.67)	6.88(7.05)	3.54(3.42)
BN_9-4 (C ₅₃ H ₅₈ N ₂ O ₆)	77.72(77.89)	7.14(7.36)	3.42(3.20)
NB_7-6 (C ₅₅ H ₆₂ N ₂ O ₆)	77.98(78.18)	7.38(7.44)	3.31(3.25)
NB_9-6 (C ₅₇ H ₆₆ N ₂ O ₆)	78.23(78.36)	7.60(7.78)	3.20(3.11)
NB_7-4 (C ₅₁ H ₅₄ N ₂ O ₆)	77.44(77.59)	6.88(7.05)	3.54(3.38)
NB_9-4 (C ₅₃ H ₅₈ N ₂ O ₆)	77.72(77.92)	7.14(7.28)	3.42(3.28)
BPB_7-6 (C ₅₉ H ₆₆ N ₂ O ₆)	78.81(79.02)	7.40(7.63)	3.42(3.37)
BPB_9-6 (C ₆₁ H ₇₀ N ₂ O ₆)	79.02(79.26)	7.61(7.83)	3.02(2.95)
BPB_7-4 (C ₅₅ H ₅₈ N ₂ O ₆)	78.36(78.22)	6.93(6.78)	3.42(3.39)
BPB_9-4 (C ₅₇ H ₆₂ N ₂ O ₆)	78.59(78.82)	7.17(7.34)	3.22(3.17)

Table S3. Analytical data for the new dimeric compounds comprising NS and BPS mesogenic unit

Dimer	Analysis: Calc(Found)/%		
	C	H	N
NS_7-6 (C ₅₅ H ₆₂ N ₂ O ₈)	75.14(75.28)	7.11(7.19)	3.19(3.12)
NS_9-6 (C ₅₇ H ₆₆ N ₂ O ₈)	75.47(75.63)	7.33(7.45)	3.09(3.01)
NS_7-4 (C ₅₁ H ₅₄ N ₂ O ₈)	74.43(74.31)	6.61(6.70)	3.40(3.28)
NS_9-4 (C ₅₃ H ₅₈ N ₂ O ₈)	74.80(74.98)	6.87(7.06)	3.29(3.22)
BPS_7-6 (C ₅₉ H ₆₆ N ₂ O ₈)	76.10(76.28)	7.14(7.32)	3.01(2.87)
BPS_9-6 (C ₆₁ H ₇₀ N ₂ O ₈)	76.38(76.47)	7.36(7.54)	2.92(2.81)
BPS_7-4 (C ₅₅ H ₅₈ N ₂ O ₈)	75.49(75.64)	6.68(6.81)	3.20(3.09)
BPS_9-4 (C ₅₇ H ₆₂ N ₂ O ₈)	75.81(75.98)	6.92(7.05)	3.10(3.14)

Table S4. Electrostatic potential distribution in kJmol^{-1} calculated for the monomers, representing each type of mesogenic core

Monomer	kJmol^{-1}

BB	-133.14	133.14
BN	-133.79	133.79
BPB	-132.93	132.93
NB	-132.95	132.95
BS	-150.86	150.86
BPS	-153.10	153.10
NS	-151.62	151.62