Synthesis of Mesomorphic 3,5-*Bis*(3,4,5-trialkyloxybenzoylamino)-4-methylbenzoates Involving Intermolecular Hydrogen Bonding

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A series of methyl 3,5-*bis*(3,4,5-trialkyloxybenzoylamino)-4-methylbenzoates (alkyl = $CH_3(CH_2)_{n-1}$, n = 8, 10, 12, 14 and 16) exhibits mesomorphic behavior at temperatures between 120 and 240 ºC. The liquid crystalline properties have been characterized using differential scanning calorimetry, optical polarization microscopy and X-ray diffraction. The molecules stack in columns which pack under hexagonal symmetry. Variable temperature infra-red absorption measurements provide evidence of intermolecular hydrogen bonding between the amide entities in both the crystalline and liquid-crystalline phases.

INTRODUCTION

Liquid crystals [1] in which hydrogen-bonding [2] adds an extra dimension of control to the structure and dynamics of the mesophases are of considerable promise as new materials [3]. Hydrogen bonding can induce association of the same or different molecules and mesophases involving both forms are known, though the present work is concerned solely with a new group of homomolecular liquid crystals derived from a series of methyl 3,5-*bis*(3,4,5-trialkyloxybenzoylamino)-4-methyl benzoates. The compounds prepared (**4**$_n$; Scheme 1), each having six substitutent alkyl 'tails', are related to similar compounds with only four alkyl tails known to form columnar liquid crystals [4,5]. The target molecules **4**$_n$ were prepared according to Scheme 2.

EXPERIMENTAL

Synthesis of Target Molecules 4$_n$

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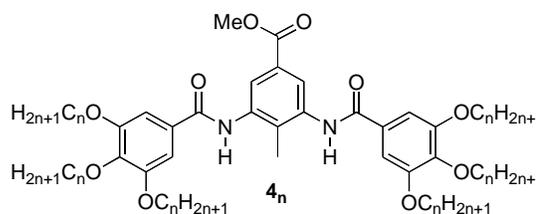
Scheme 1. The target molecules **4**$_n$ with six alkyl chain substituents

4-Methyl-3,5-bis-(3,4,5-tris-octyloxy-benzoylamino)-benzoic acid methyl ester (4$_8$). This compound was prepared from methyl 3,5-diamino-4-methyl-benzoate (0.310 g, 1.72 mmol), **3**$_8$ (1.83 g, 3.48 mmol) and K_2CO_3 in excess (2.500 g, 18.1 mmol) in dry acetone (50 ml). This reaction gave 1.630 g (1.41 mmol) of **4**$_8$ (82%, Mw = 1157.69 g). ^1H NMR (CDCl$_3$) δ (ppm) = 0.87 (t, ^3J = 6.7 Hz, 18H, CH$_3$), 1.30 (m-br, 48H, CH$_2$), 1.49 (m-br, 12H, OCH$_2$CH$_2$CH_2), 1.80 (m-br, 12H, OCH$_2$CH_2), 2.23 (s, 3H, CH$_3$ benzyl), 3.88 (s, 3H, OCH$_3$),
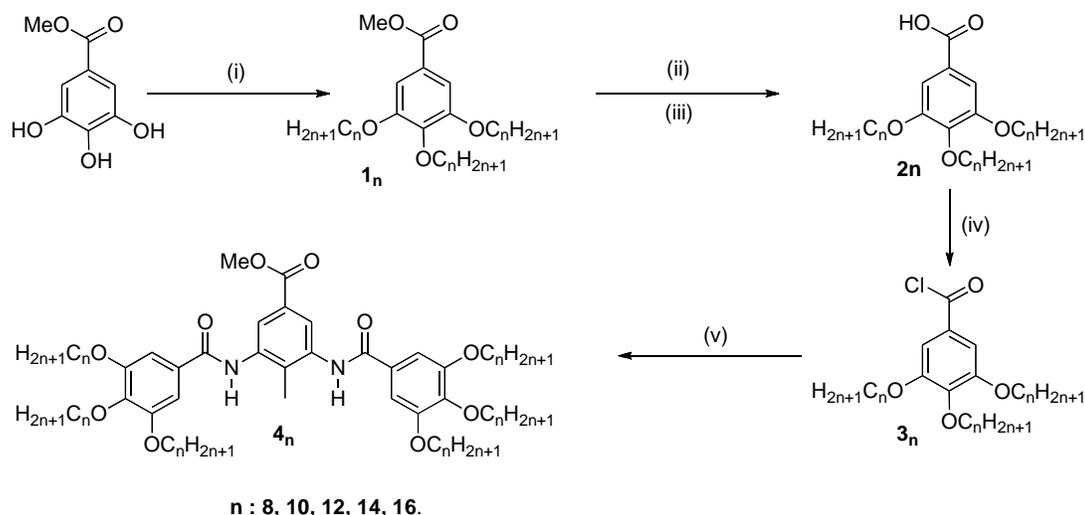
Scheme 2. (i) BrC_nH_{2n+1}, K_2CO_3 excess, DMF reflux overnight ; (ii) 2 equiv. KOH, EtOH reflux overnight; (iii) H_3O^+, H_2O; (iv) $SOCl_2$ reflux 2h; (v) 0.5 equiv. 3,5-diamino-4-methylbenzoic acid methyl ester, dry acetone or chloroform, 10% NEt_3, 4h.

4.04 (m-br, 12H, OCH_2), 7.13 (s, 4H, aromatic.), 7.86 (s, 2H, aromatic or NH), 8.15 (s, 2H, aromatic or NH). ^{13}C {^1H} NMR ($CDCl_3$) δ (ppm) = 13.66, 14.04, 22.65, 25.98, 26.08, 29.27, 29.37, 29.52, 30.35, 31.81, 31.88, 52.08, 69.33, 73.52, 76.58, 77.00, 77.43, 106.07, 123.94, 128.11, 128.68, 133.20, 136.48, 141.69, 153.21, 166.12, 166.15. FT-IR (KBr celldisc, cm^{-1}) 3183 (br-m), 2920 (s), 2850 (m), 1728 (s), 1635 (s), 1494 (s), 1467 (s), 1338 (s), 1228 (s). Anal. Calc. For $C_{71}H_{116}N_2O_{10}$: C, 73.66; H, 10.10; N, 2.42. Found: C, 73.57; H, 9.96; N, 2.38.

4-Methyl-3,5-*bis*-(3,4,5-tris-decyloxy-benzoylamino)-benzoic acid methyl ester (4_{10}). This compound was prepared from methyl 3,5-diamino-4-methyl-benzoate (0.299g, 1.66 mmol), 3_{10} (2.060g, 3.38 mmol) and K_2CO (2.500 g, 18.1 mmol) in dry acetone (50 ml). The reaction led to 1.630 g (1.23 mmol) of 4_{10} (74%, Mw = 1326.01 g). ^1H NMR ($CDCl_3$) δ (ppm) = 0.88 (t, ^3J = 6.7 Hz, 18H, CH_3), 1.27 (m-br, 72H, CH_2), 1.49 (m-br, 12H, $OCH_2CH_2CH_2$), 1.80 (m-br, 12H, OCH_2CH_2), 2.25 (s, 3H, CH_3 benzyl), 3.88 (s, 3H, OCH_3), 4.04 (m-br, 12H, OCH_2), 7.12 (s, 4H, aromatic), 7.80 (s, 2H, aromatic or NH), 8.12 (s, 2H, aromatic or NH). ^{13}C {^1H} NMR ($CDCl_3$) δ (ppm) = 13.71, 14.07, 22.66, 25.98, 26.12,

29.55, 30.36, 31.91, 52.11, 69.38, 73.54, 76.57, 77.00, 77.20, 77.42, 106.08, 123.83, 128.26, 128.72, 132.96, 136.52, 141.75, 153.25, 166.09, 166.13. FT-IR (KBr celldisc, cm^{-1}) 3178 (br-m), 2920 (s), 2850 (m), 1728 (s), 1635 (s), 1494 (s), 1467 (s), 1338 (s), 1228 (s). Anal. Calcd. For $C_{83}H_{140}N_2O_{10}$: C, 75.18; H, 10.64; N, 2.11. Found: C, 75.06; H, 10.53; N, 2.10.

4-Methyl-3,5-*bis*-(3,4,5-tris-dodecyloxy-benzoylamino)-benzoic acid methyl ester (4_{12}). This compound was prepared from methyl 3,5-diamino-4-methyl-benzoate (0.191 g, 1.060 mmol), 3_{12} (1.510 g, 2.24 mmol) and K_2CO_3 (2.500 g, 18.1 mmol) in chloroform (50 ml). The reaction gave 1.550 g (1.04 mmol) of 4_{12} (98%, Mw = 1494.33 g). ^1H NMR ($CDCl_3$) δ(ppm) = 0.88 (t, ^3J = 6.7 Hz, 18H, CH_3), 1.27 (m-br, 96H, CH_2), 1.49 (m-br, 12H, OCH_2CH_3), 1.80 (m-br, 12H, OCH_2CH_2), 2.25 (s, 3H, CH_3 benzyl), 3.88 (s, 3H, OCH_3), 4.04 (m-br, 12H, OCH_2), 7.12 (s, 4H, aromatic), 7.84 (s, 2H, aromatic or NH), 8.13 (s, 2H, aromatic or NH). ^{13}C {^1H} NMR ($CDCl_3$) δ (ppm) = 13.66, 14.04, 22.64, 25.98, 26.11, 29.53, 30.35, 31.89, 52.05, 69.29, 73.50, 76.56, 76.99, 77.19, 77.41, 106.07, 124.11, 127.96, 128.59, 133.63, 136.46, 141.62, 153.16, 166.09, 166.23. FT-IR (KBr celldisk, cm^{-1}) 3178 (br-m), 2920 (s), 2850 (m), 1728 (s), 1635 (s), 1494 (s),

1467 (s), 1338 (s), 1228 (s). Anal. Calcd. For $C_{95}H_{164}N_2O_{10}$: C, 76.36; H, 11.06; N, 1.87. Found: C, 76.32; H, 11.03; N, 1.85.

4-Methyl-3,5-*bis*-(3,4,5-tris-tetradecyloxy-benzoyl-amino)-benzoic acid methyl ester (4$_{14}$). This compound was prepared from methyl 3,5-diamino-4-methyl-benzoate (0.183 g, 1.016 mmol), 3$_{14}$ (1.700 g, 2.19 mmol) and K_2CO_3 (2.500 g, 18.1 mmol) in chloroform (50 ml). The reaction led to 1.570 g (0.944 mmol) of 4$_{14}$ (93%, Mw = 1662.65 g). ^1H NMR (CDCl$_3$) δ (ppm) = 0.89 (t, ^3J = 6.7 Hz, 18H, CH_3), 1.27 (m-br, 120H, CH_2), 1.49 (m-br, 12H, OCH$_2$CH$_2$CH_2), 1.80 (m-br, 12H, OCH$_2$CH_2), 2.25 (s, 3H, CH_3 benzyl), 3.89 (s, 3H, OCH_3), 4.04 (m-br, 12H, OCH_2), 7.12 (s, 4H, aromatic), 7.80 (s, 2H, aromatic or NH), 8.15 (s, 2H, aromatic or NH). ^{13}C {^1H} NMR (CDCl$_3$) δ (ppm) = 13.70, 14.05, 22.65, 26.10, 29.53, 30.34, 31.89, 52.10, 69.34, 73.52, 76.55, 76.97, 77.39, 106.01, 123.81, 128.20, 128.69, 133.00, 136.48, 141.69, 153.21, 166.09. FT-IR (KBr celldisk, cm^{-1}) 3178 (br-m), 2920 (s), 2850 (m), 1728 (s), 1635 (s), 1494 (s), 1467 (s), 1338 (s), 1228 (s). Anal. Calcd. For $C_{107}H_{188}N_2O_{10}$: C, 77.30; H, 11.40; N, 1.68. Found: C, 77.25; H, 11.34; N, 1.65.

4-Methyl-3,5-*bis*-(3,4,5-tris-hexadecyloxy-benzoyl-amino)-benzoic acid methyl ester (4$_{16}$). This compound was prepared from methyl 3,5-diamino-4-methyl-benzoate (0.174 g, 0.966 mmol), 3$_{16}$ (1.700 g, 1.973 mmol) and K_2CO_3 (2.500 g, 18.1 mmol) in chloroform (50 ml). The reaction gave 1.767 g (0.996 mmol) of 4$_{16}$ (99%, Mw = 1830.96 g). ^1H NMR (CDCl$_3$) δ (ppm) = 0.88 (t, ^3J = 6.7 Hz, 18H, CH_3), 1.26 (m-br, 144H, CH_2), 1.49 (m-br, 12H, OCH$_2$CH$_2$CH_2), 1.79 (m-br, 12H, OCH$_2$CH_2), 2.27 (s, 3H, CH_3 benzyl), 3.90 (s, 3H, OCH_3), 4.04 (m-br, 12H, OCH_2), 7.11 (s, 4H, aromatic), 7.74 (s, 2H, aromatic or NH), 8.18 (s, 2H, aromatic or NH). ^{13}C {^1H} NMR (CDCl$_3$) δ (ppm) = 14.09, 22.68, 26.12, 29.54, 30.36, 31.93, 52.19, 69.46, 73.59, 76.58, 77.00, 77.19, 77.42, 106.04, 123.58, 128.59, 128.83, 132.35, 136.46, 141.84, 153.31, 165.98, 166.16. FT-IR (KBr celldisk, cm^{-1}) 3174 (br-m), 2920 (s), 2850 (m), 1728 (s), 1635 (s), 1494 (s), 1467 (s), 1338 (s), 1228 (s). Anal. Calcd. For $C_{119}H_{212}N_2O_{10}$: C, 78.06; H, 11.67; N, 1.53. Found: C, 77.97; H, 11.63; N, 1.51.

RESULTS AND DISCUSSION

The desire to incorporate metal binding units, such as polypyridine entities, into a mesogen, a functionalization possible but known to cause the loss of liquid crystalline behavior in the four-tailed compounds, led us to the present investigation of six-tailed compounds. The target molecules 4$_n$ were prepared according to Scheme 2. Compounds 1$_n$, 2$_n$, and 3$_n$ were prepared by literature procedures [4]. Reaction of acid chlorides 3$_n$ with methyl 3,5-diamino-4-methylbenzoate leads to the products 4$_n$ in excellent yields (74-99% for the last step).

All compounds 4$_n$ were characterized by ^1H NMR, ^{13}C{^1H} NMR and FT-IR measurements. The FT-IR studies show the presence of ester and amide groups (ν(CO ester) = 1728 cm^{-1}; ν(CO amide) = 1635 cm^{-1}). The aromatic amide NH stretching bands appear in the IR spectra near 2174 cm^{-1}. This is consistent with the involvement of this entity in H-bonding, presumed to be intermolecular in nature, since the 4-methyl substituent on the benzamide ring was incorporated to prevent intramolecular interaction [6]. The ^1H NMR (CDCl$_3$) resonance of this sterically active methyl group appears at δ 2.24. The thermotropic liquid crystalline behavior of the compounds 4$_n$ was investigated using differential scanning calorimetry (Perkin-Elmer DSC7, heating and cooling rates of 10 K min^{-1}), polarizing optical microcoscopy (Leitz-Orthoplan, Mettler FP82 hot stage) and X-ray diffraction (XRD) (Guinier focusing camera, CuKα_1 radiation, powder samples in Lindemann capillaries, INSTEC hot stage, INEL CPS-120 curved position-sensitive detector). The results of these measurements are summarized in Fig. 1.

Phase changes between the solid and liquid crystalline materials were clearly defined by sharp peaks in the DSC thermograms, with less marked enthalpy changes characterizing the liquid-crystal to the isotropic liquid transitions. All compounds except 4$_8$ exist as two solid polymorphs in the temperature range studied, and all form a single hexagonal columnar mesophase. Optical textures with pseudo-focal-conic forms (Fig. 2), observed by microscopy on slow cooling of the isotropic melts, are strongly suggestive of a columnar structure, as was definitely established by X-ray diffraction measurements.

Thus, the diffraction patterns recorded at high temperature (Fig. 3) display three sharp small-angle reflections with reciprocal spacings in the ratio 1: $\sqrt{3}$: $\sqrt{4}$, indicative of hexagonal packing of indefinitely long columns. A least-squares double-Gaussian fit of the experimental data shows that the wide angle scattering of the hexagonal columnar phase
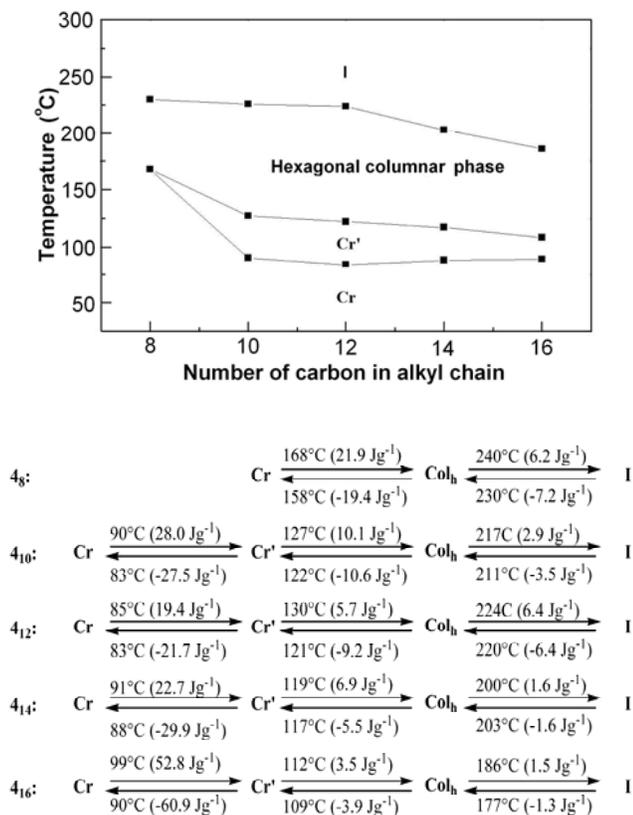
Fig. 2. Optical texture of compound **4₈** observed with a Polarizing microscope on slow cooling from the isotropic melt: pseudo-focal-conic texture at 223 °C.

4₈: Cr $\xrightleftharpoons[\text{158°C (-19.4 Jg}^{-1})]{\text{168°C (21.9 Jg}^{-1})}$ Col$_h$ $\xrightleftharpoons[\text{230°C (-7.2 Jg}^{-1})]{\text{240°C (6.2 Jg}^{-1})}$ I

4₁₀: Cr $\xrightleftharpoons[\text{83°C (-27.5 Jg}^{-1})]{\text{90°C (28.0 Jg}^{-1})}$ Cr' $\xrightleftharpoons[\text{122°C (-10.6 Jg}^{-1})]{\text{127°C (10.1 Jg}^{-1})}$ Col$_h$ $\xrightleftharpoons[\text{211°C (-3.5 Jg}^{-1})]{\text{217°C (2.9 Jg}^{-1})}$ I

4₁₂: Cr $\xrightleftharpoons[\text{83°C (-21.7 Jg}^{-1})]{\text{85°C (19.4 Jg}^{-1})}$ Cr' $\xrightleftharpoons[\text{121°C (-9.2 Jg}^{-1})]{\text{130°C (5.7 Jg}^{-1})}$ Col$_h$ $\xrightleftharpoons[\text{220°C (-6.4 Jg}^{-1})]{\text{224C (6.4 Jg}^{-1})}$ I

4₁₄: Cr $\xrightleftharpoons[\text{88°C (-29.9 Jg}^{-1})]{\text{91°C (22.7 Jg}^{-1})}$ Cr' $\xrightleftharpoons[\text{117°C (-5.5 Jg}^{-1})]{\text{119°C (6.9 Jg}^{-1})}$ Col$_h$ $\xrightleftharpoons[\text{203°C (-1.6 Jg}^{-1})]{\text{200°C (1.6 Jg}^{-1})}$ I

4₁₆: Cr $\xrightleftharpoons[\text{90°C (-60.9 Jg}^{-1})]{\text{99°C (52.8 Jg}^{-1})}$ Cr' $\xrightleftharpoons[\text{109°C (-3.9 Jg}^{-1})]{\text{112°C (3.5 Jg}^{-1})}$ Col$_h$ $\xrightleftharpoons[\text{177°C (-1.3 Jg}^{-1})]{\text{186°C (1.5 Jg}^{-1})}$ I

Fig. 1. (left) Transition temperatures of the compounds as a function of the number of carbon atoms in the alkyl chains (Cr and Cr' = crystal phase, I = isotropic liquid); (right) phase transition temperatures (°C) and corresponding enthalpy values (J g^{-1}) in parentheses recorded upon third heating and cooling obtained by differential scanning calorimetry as a function of the number of atoms in the alkyl chains (Col$_h$ = hexagonal columnar liquid crystal phase).

Fig. 3. X-ray diffraction pattern of the columnar phase of **4₁₆** at 160 °C. For clarity, the intensities at Bragg angle 2θ ≥ 4.5° are multiplied fifteenfold.

results from the superposition of three distinct rings. One diffuse ring (**B**) with d 4.70 Å related to the disordered conformation of the alkyl chains (liquid like), one ring (**C**) with d 3.75 Å corresponding to aromatic rings stacked together to form columns and one more diffuse peak (**A**), $d \approx$ 8 Å, corresponding to stacked aromatic-ring trimers (d 2* 3.75 Å) formed in the column [7]. The latter separations are consistent with aromatic unit association induced by amide H-bonding, weak pi-pi interactions and the formation of trimers.
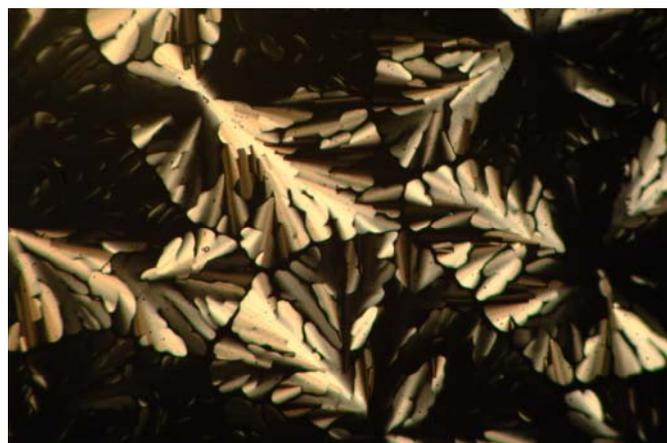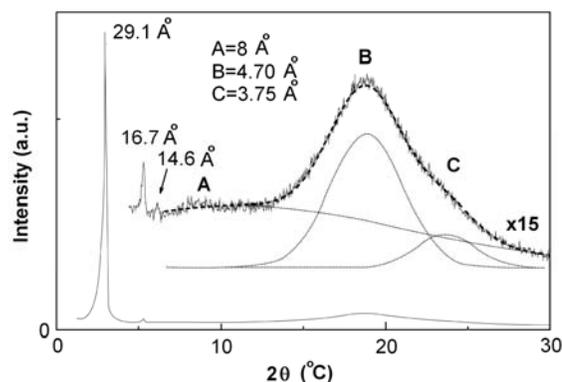
This trimeric unit has already been established by single crystal X-ray diffraction on a compound containing similar aromatic part substituted by a phenanthroline [4]. Additionally, we have investigated for all the compounds **4ₙ** the temperature dependence of the intercolumnar distances of the hexagonal columnar phase (Fig. 4). As expected, the intercolumnar distance increases as a function of the length of the alkyl chains.

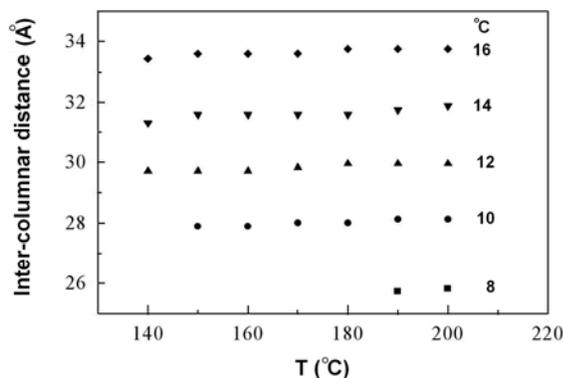Measuring the IR spectra as a function of temperature (Fig.

Fig. 4. Temperature dependence of the hexagonal unit cell parameters of 4_n in the columnar state: intercolumnar distance.

5) revealed the presence of different H-bonding networks in the crystal and liquid-crystal phases [6]. It is clear that significant changes occur in the NH stretching band between crystal and liquid-crystal phases. This band shifts towards higher wave numbers as the temperature is increased, a situation entirely consistent with intermolecular hydrogen-bonding between the amide functions being weaker in the mesomorphic than in the solid state.
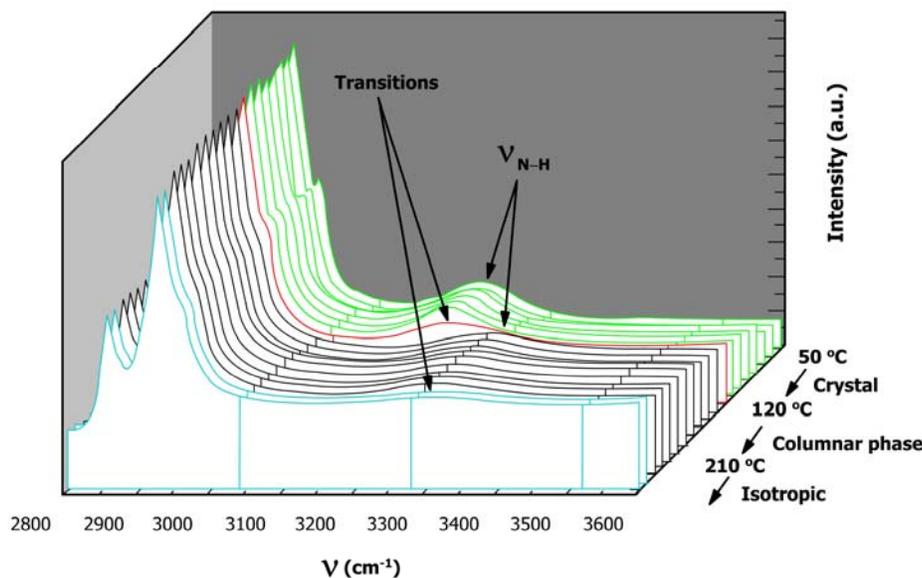
CONCLUSIONS

In conclusion, all members of a new series of methyl 3,5-*bis*(3,4,5-trialkyloxybenzoylamino)-4-methylbenzoates (alkyl = $CH_3(CH_2)_{n-1}$, n = 8, 10, 12, 14 and 16) form a single mesophase over a similar temperature range. This mesophase involves hexagonal packing of columnar associates in which the unit spacing is consistent with interactions through intermolecular hydrogen-bonding involving amide groups and p-p stacking of the aromatic entities.

ACKNOWLEDGMENTS

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Fig. 5. FTIR spectra recorded for the 4_{12} compound from 50 °C to 230 °C with steps of 10 °C. Green frames define the crystal state, red the crystal to liquid-crystal transition and blue the isotropic liquid.

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