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New mesogenic compounds having fork-like or cyclic amide terminal groups

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Two homologous series of mesogenic materials with molecules containing an amide moiety, cyclic or symmetrically branched, as the terminal group have been synthesized. Materials of both series form lamellar liquid crystal phases. It was observed that elongation of the amide chains in 'fork-like' compounds destabilizes the mesophases, while 'cyclic' materials, even with quite large terminal amide rings, exhibit enantiotropic liquid crystalline phases.

1. Introduction

Fork-like or swallow-tailed compounds are a special class of mesogenic materials containing branched terminal substituents, usually with large branches. Recently some unusual polymorphism has been reported for bi-swallow-tailed materials. Weissflog and co-authors have described a series of compounds which exhibit both lamellar and columnar mesomorphism [1]. In some compounds even a re-entrant isotropic phase was observed [2]. In most of these series, the branched terminal parts of the molecule are derived from the appropriate alcohol and attached to the mesogenic core by an ester linkage. Here we present the mesogenic properties of compounds in which the *N,N*-dialkyl-amide moiety was used as the terminal group. These are compared with materials having a cyclic amide group in the molecule, for which it has been found that the large flexible rings fold to give rod-like molecules suitable for lamellar packing.

2. Experimental and synthesis

The identification of the mesophases was based on microscopic observations of characteristic textures using a Nikon Ophthot-2-Pol polarizing microscope equipped with a Mettler FP82HT heating stage. Phase transition

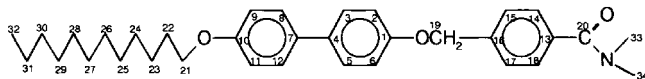
temperatures and associated thermodynamic parameters were taken from calorimetric measurements performed with a Perkin-Elmer DSC7 differential scanning calorimeter. The X-ray studies were done using a modified DRON system equipped with Ge monochromator, working in reflection mode. The diffractometer was controlled by software developed in the LabView environment. Samples were prepared on a glass slide with one free surface assuring homeotropic alignment.

The synthetic route for the target compounds is outlined in the scheme. The synthetic procedure giving compound **A** has already been described elsewhere [3].

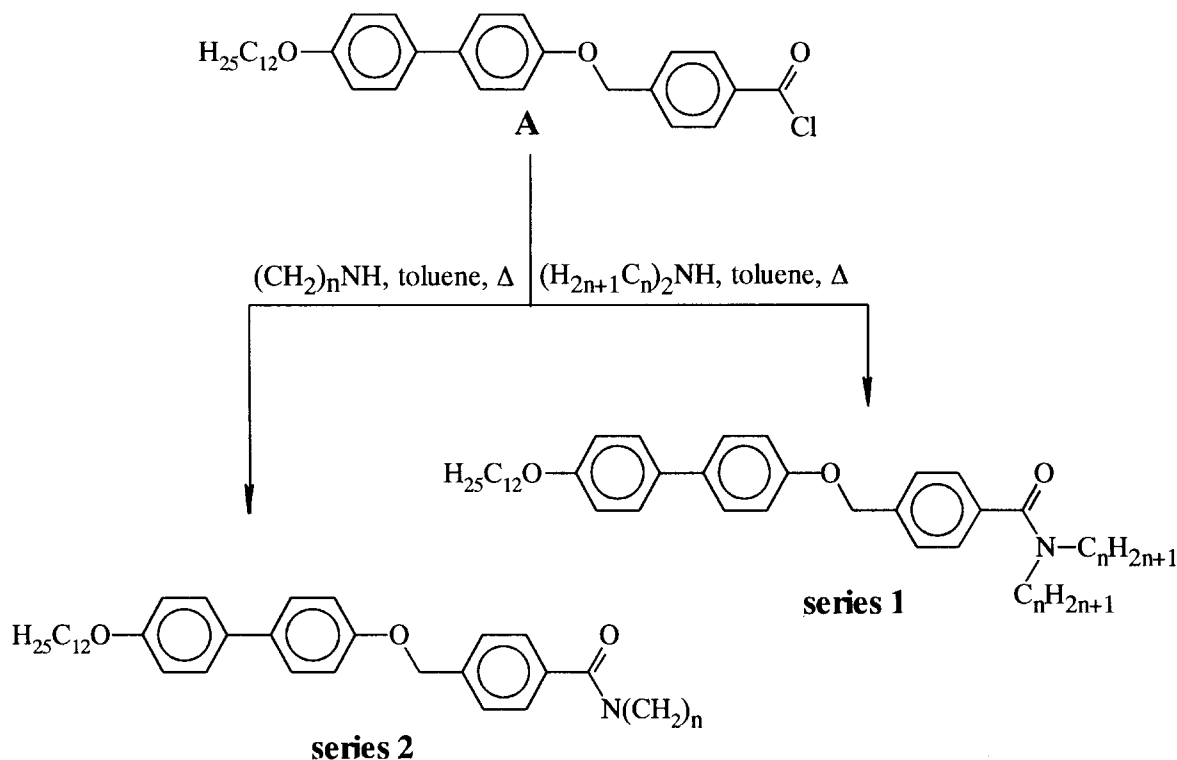
The acid chloride **A** was added to the appropriate amine (molar ratio = 2:1) dissolved in toluene. The reaction mixture was stirred and heated at 80°C for 2 h; on cooling, the precipitate was filtered off. The filtrate was reduced in volume and the crude product purified by column chromatography on silica gel using toluene as eluent. Yields varied from 85 to 90%.

The structures of the products were confirmed by elemental analysis, IR spectroscopy, and ¹H and ¹³C NMR spectroscopy, as shown in the following example.

N,N-dimethyl-4-(4'-dodecyloxy biphenyl-4-yl)oxymethyl)-benzamide:



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Scheme.

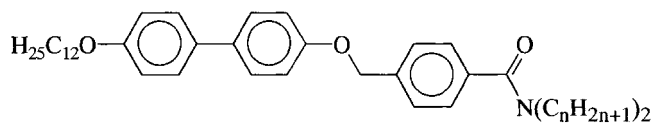
Elemental analysis for $\text{C}_{34}\text{H}_{45}\text{NO}_3$: calc. C 79.18, H 8.79, N 2.72; found C 79.20, H 8.80, N 2.70%. IR ν_{max} (KBr)/ cm^{-1} : 2980, 2950, 2900, 2850, 2810, 1700, 1600, 1510, 1280, 1250. ^1H NMR (δ , CDCl_3): 0.88 (t, 3H, CH_3 (32), $J = 6.6$ Hz); 1.27–1.45 (m, 18H, CH_2 (23–31)); 1.80 (quintet, 2H, CH_2 (22), $J = 6.6$ Hz); 3.00 (bs, 3H, CH_3 (33 or 34)); 3.11 (bs, 3H, CH_3 (33 or 34)); 3.98 (t, 2H, CH_2 (21), $J = 6.6$ Hz); 5.12 (s, 2H, CH_2 (19)); 6.94 (dd, 2H, $\text{H}_9, \text{H}_{11}$, $J_{9,8} = J_{11,12} = 8.5$ Hz, $J_{9,11} = 2.5$ Hz); 7.01 (dd, 2H, $\text{H}_7, \text{H}_{13}$, $J_{7,6} = J_{13,14} = 8.5$ Hz, $J_{7,13} = 2.5$ Hz); 7.46 (dd, 2H, $\text{H}_6, \text{H}_{12}$, $J_{6,5} = J_{12,11} = 8.5$ Hz, $J_{6,12} = 2.5$ Hz); 7.47 (dd, 2H, $\text{H}_8, \text{H}_{10}$, $J_{8,9} = J_{10,11} = 8.5$ Hz, $J_{8,10} = 2.5$ Hz); 7.48 (dd, 2H, $\text{H}_{15}, \text{H}_{17}$, $J_{15,14} = J_{17,18} = 8.0$ Hz, $J_{15,17} = 2.0$ Hz); 7.49 (dd, 2H, $\text{H}_{14}, \text{H}_{16}$, $J_{14,15} = J_{16,17} = 8.0$ Hz, $J_{14,16} = 2.0$ Hz). ^{13}C NMR (δ , CDCl_3): 14.13; 22.70; 26.07; 29.31; 29.362; 29.42; 29.61; 29.65; 31.93; 35.43; 39.62; 68.11; 69.61; 114.77; 115.11; 127.22; 127.43; 127.70; 127.76; 133.09; 134.04; 135.91; 138.63; 157.64; 158.35; 171.34.

3. Results and discussion

Phase transition temperatures and associated enthalpy changes are collected in tables 1 and 2 for series 1 (fork-like) and series 2 (cyclic), respectively. The corresponding phase diagrams are shown in figure 1. Compounds of both series form lamellar phases, mainly the fluid smectic A and C phases. In series 1 the material with $n = 8$ also exhibits the nematic phase, which is surprising as

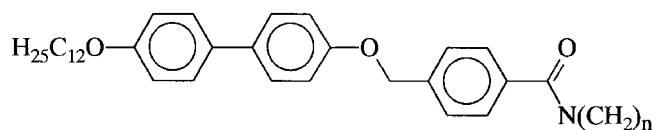
generally nematic phases are observed for the short chain homologues in a given series. For the shortest homologue of this series ($n = 1$) below the SmA phase a crystal B phase appears, while for the next homologue ($n = 2$), in addition to the SmA and SmC phases, tilted smectic phases of higher intralayer ordering are detected, specifically, the HexF and CrG phases. A similarly sharp discrimination between orthogonal and tilted phases was also observed for the related compounds having an ester group instead of the amide link [3]. In series 2 all the compounds display the SmA phase and in addition four exhibit the tilted smectic C phase. Only one homologue ($n = 5$) forms the more ordered, hexatic smectic F phase. However, it should be noted that in both homologous series all the higher ordered phases are monotropic and could be observed only on supercooling. In series 1 from the $n = 4$ homologue all liquid crystalline phases are monotropic.

Mesophases were identified from their optical textures observed with a polarizing microscope. Smectic A phases formed a focal-conic fan texture with smooth fans when the material was sandwiched between two glass slides, or the homeotropic texture when the sample had one free surface. The phase transition from SmA to CrB was accompanied by the appearance of characteristic transition bars on the fan texture, and no changes were observed to the homeotropic texture. For materials exhibiting the SmA–SmC phase transition, the breaking

Table 1. Phase transition temperatures ($^{\circ}\text{C}$) and, in parentheses, the associated enthalpy changes (J g^{-1}) for series 1.

n	Cr	CrB	CrG	HexF	SmC	SmA	N	I
1	• 162.7 (87.4)	• 158.6 (5.8)				• 168.1 (26.3)		•
2	• 87.7 (53.9)		• 72.9 (2.4)	• 82.9 (3.7)	• 102.7	• 130.5 (16.1)		•
3	• 92.4 (100.2)				• $\sim 70^a$	• 101.4 (8.1)		•
4	• 86.5 (68.5)					• 84.6 (6.1)		•
8	• 71.6 (9.6)					• 59.7 (0.3)	• 63.2 (1.7)	•

^a From microscopic observation.

Table 2. Phase transition temperatures ($^{\circ}\text{C}$) and, in parentheses, the associated enthalpy changes (J g^{-1}) for series 2.

n	Cr	HexF	SmC	SmA	I
3	• 168.7 (62.3)			• 189.8 (27.1)	•
4	• 162.4 (97.2)			• 157.9 (20.6)	•
5	• 115.6 (50.4)	• 99.1 (2.7)	• 104.0 (0.6)	• 141.0 (16.3)	•
6	• 123.3 (29.8)		• 97.6 (0.7)	• 127.2 (8.8)	•
7	• 103.5 (40.3)			• 112.3 (10.1)	•
8	• 94.6 (23.7)		• 84.5 (1.6)	• 105.8 (8.6)	•
12	• 87.1 (51.5)		• 71.3 (0.05)	• 119.1 (9.0)	•

of the fans and the appearance of colourful spots on them were observed; from the homeotropic texture of the SmA phase a schlieren texture developed. The texture of the HexF phase obtained on cooling the SmC phase was either (i) broken fans with well defined breaks forming characteristic 'L-shapes' or (ii) a smooth schlieren type texture which developed from the schlieren texture of the SmC phase. The CrG phase was identified from its mosaic texture. The assignment of mesophases was also confirmed by the shapes of the signals obtained in the DSC studies. The transition from the smectic C phase to the hexatic HexF phase was accompanied by strong pretransitional heat capacity anomalies visible on the thermograms as broad wings or a cusp-like peak [4]. The transition to the crystalline phases (CrG or CrB) was observed as a sharp peak with typical values of enthalpy changes.

Given the tendency for the strong destabilization of mesophase in homologues of series 1 on increasing the terminal chain length attached to the nitrogen atom, it could be supposed that the molecules in the phase become less rod-like. This could be caused by an inclination of one of the chains away from the mesogenic core axis, making the molecular shape less anisotropic.

In order to obtain information concerning the conformations of the amide group chains, X-ray measurements of the layer spacings in the SmA phases were performed. We compared the results for $n = 3$ of series 1 with the corresponding member of series 2 ($n = 6$) for which the effective length of the cyclic and alkyl terminal groups are comparable (figure 2). It was found that the layers in the SmA phase of the fork-like compound are about 1 \AA thicker than in the corresponding cyclic substance. However, the ratio of layer spacing (d) to the

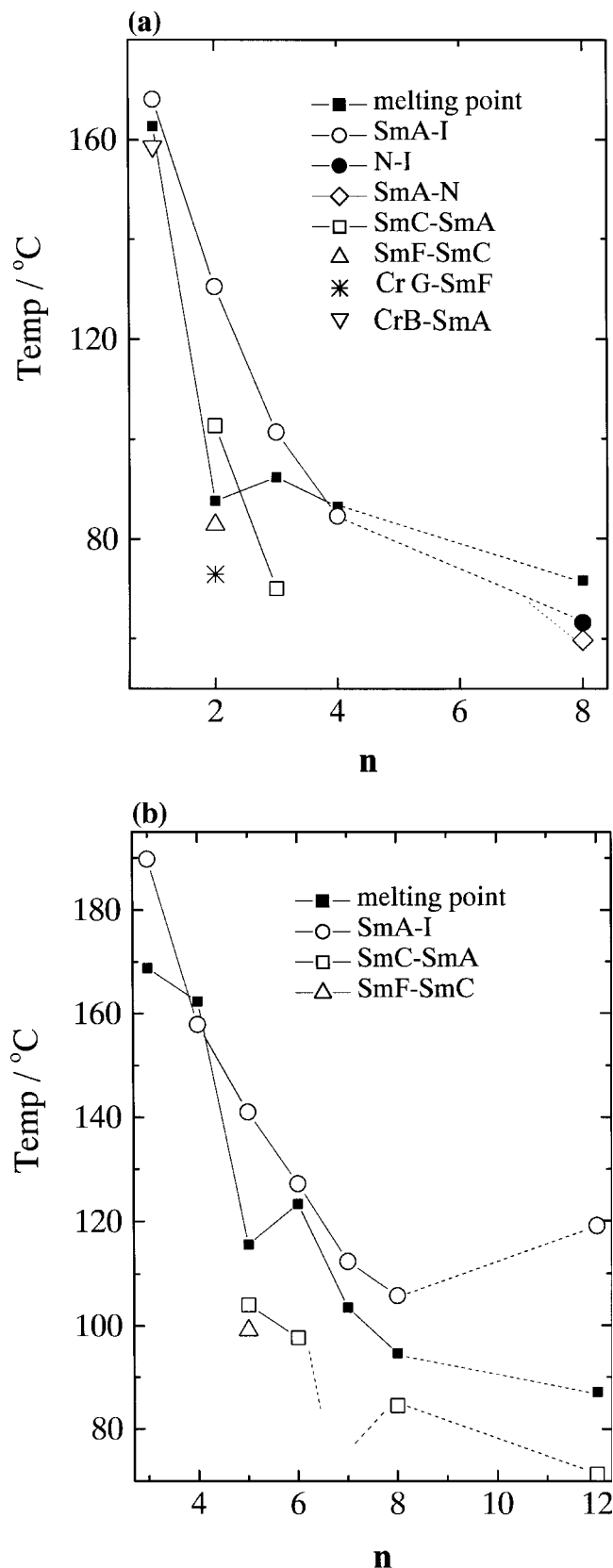


Figure 1. Phase diagrams for series 1 (a), and series 2 (b).

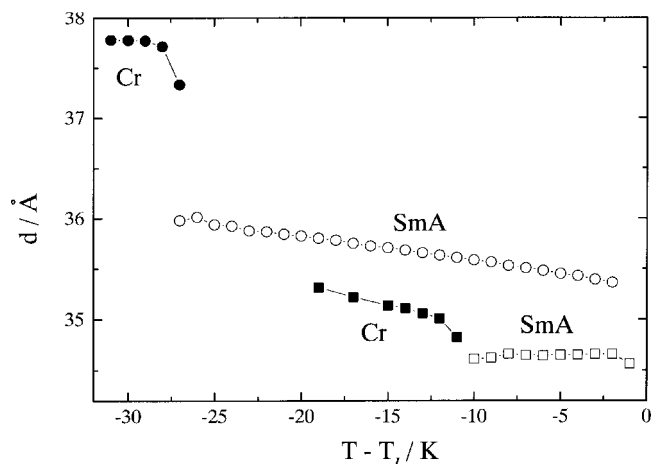


Figure 2. Temperature dependence of the layer spacing for $n=3$ of series 1 (circles) and $n=6$ of series 2 (squares). Solid points show data recorded in the crystalline phase.

molecular length (L) in the most stretched conformation is identical in both materials. The measured values, $d/L = 0.93$ – 0.95 for a compound of series 1 and $d/L = 0.95$ for a compound of series 2, are typical for the smectic A phase. This indicates that the orientational order parameter is similar for both substances.

The larger layer thickness observed for the compound of series 1 suggests that one of the chains of the fork-like moiety should be longer than its cyclic counterpart and directed along the core, so increasing the molecular length. This can happen if one of the chains adopts an all-*trans* conformation, so extending the long molecular axis. In such a case the other chain can be supposed to be significantly inclined from the long molecular axis because of the presence of *gauche* conformations.

In series 2, a strong dependence of the melting and clearing temperatures on the size of the terminal amide ring is observed for short homologues. This can be related to the rigidity of small (e.g. 4-member) rings. Thus attaching the ring to the mesogenic core can actually be treated as an elongation of the rigid part of the molecule, which results in an increase in the isotropization temperature. Larger amide rings are relatively flexible and thus placing them at the terminal position of the mesogenic core does not increase the isotropization temperature of the material.

4. Conclusion

We have shown that an *N,N*-disubstituted amide moiety can be used as a terminal group instead of the more frequently used ester linked unit in mesogenic materials. However, the liquid crystalline phases are strongly destabilized by the elongation of the alkyl chains attached to the nitrogen atom in fork-like molecules. This seems to be caused by a broadening of

the molecule and a reduction in its shape anisotropy arising from the non-parallel alignment of one of the chains to the mesogenic core. Also the results of smectic layer spacing measurements suggest that the branched amide group can adopt conformations in which one of the chains is extended along the long molecular axis and the other is considerably inclined. For materials with cyclic terminal rings a pronounced increase in the melting and clearing temperatures for homologues having small terminal hetero-rings, and the stabilization of the transition temperatures on enlarging the amide moiety, were observed. This suggests that large cyclic groups are sufficiently flexible to be used as terminal substituents on the mesogenic core.

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