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How simple can a thermotropic mesogenic molecule be? Supramolecular layers through a network of hydrogen bonds

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How simple can a thermotropic mesogenic molecule be? Supramolecular layers through a network of hydrogen bonds

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The supramolecular approach was applied to obtain a thermotropic liquid crystalline phase from the smallest possible molecules. Diaminobenzene derivatives are able to form smectic layers through a network of interconnected hydrogen bonded rings. The observed smectic A phase exhibits unusually small optical birefringence, comparable with that of lyotropic lamellar phases.

Keywords: hydrogen bonding; supramolecular lamellar structure; liquid crystals; birefringence

1. Introduction

Mesophases are formed through various mechanisms, in which the repulsive and attractive interactions between molecules of anisotropic shape, hydrogen bonding, microsegregation, etc, play a role. In order to obtain a particular phase structure or phase properties, the molecules have to be engineered to tune the specific molecular interactions. In recent years, organic synthesis efforts have resulted in the design and creation of molecules of increasing complexity, e.g. dendritic molecules (*1*), rod–coil molecules (*2*) and polyphilic molecules (*3*). On the other hand, we can raise the question of how simple the molecule can be that forms a liquid crystalline phase. It is generally assumed that a mesogenic molecule has to have at least a two-ring core (*4*); the best known and studied examples of such molecules are cyanobiphenyl derivatives (*5*) or biphenyl carboxylates (*6*) forming either nematic or smectic phases. Although one-ring mesogenic molecules, like carboxylic acids (*7*), are also well known, their mesogenic properties are due to their ability to form hydrogen bonded dimers. Thus, even the molecule formally has a one-ring core structure, in the mesophase strongly anisotropic, three-ring core entities exist, which are responsible for the mesophase formation. A similar principle, 'dimerization' or even 'polymerization' through hydrogen bonding, was applied for a number of dissymmetric molecules bearing complementary functional groups (*8*). Small non-mesogenic molecules can be also bonded by metal ions to form larger, anisotropic mesogenic objects (*9*).

2. Experimental

Phase transition temperatures of the compounds studied and their thermal effects were determined using differential scanning calorimetry (DSC, Perkin Elmer DSC-7). Their optical properties were studied in glass cells, 3–5 μm thick, having surfactant layers for planar orientation. The cells were placed into a Mettler FP82HT hot stage for temperature control with accuracy 0.1 K. For observation of the optical textures a polarizing optical microscope (Nikon OptiPhot-2POL) was used, equipped with a digital camera. Birefringence was measured with a setup built using a He–Ne laser (JDS Uniphase, 1135P), photoelastic modulator (Hinds, PEM-90), photodiode (FLCE PIN20) and lock-in amplifier (EG&G 7265), with light propagating along the normal to the cell surface. X-ray measurements of the smectic layer spacing were performed with the modified DRON diffractometer (Cu K_α line) in the reflection mode using one surface-free sample.

Synthesis

The general route for synthesis of the studied compounds is outlined in Scheme 1.

2-Nitro-4-alkoxyacetanilides.

These compounds were obtained according to modified procedure for synthesis of 2-nitro-4-butyloxyacetanilide (*10*).

Octyloxyacetanilide (13 g, 0.05 mol) was dissolved in 50 ml AcOH and a solution of 25 ml HNO_3 (d=1.4 g cm^{-3}) in 20 ml of AcOH was added. The

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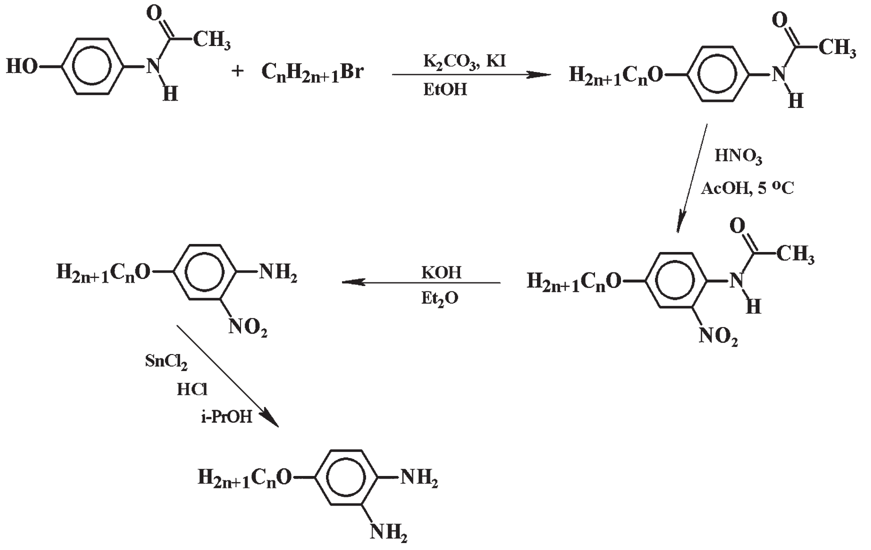

Scheme 1. Synthetic path to obtain studied compounds **C8** and **C10**.

mixture was stirred for 1 h at a temperature below 5°C. Then 300 ml of water was added. The precipitate was filtered off and washed with water. The crude product was crystallised from hexane to obtain yellow crystals of 2-nitro-4-octyloxyacetanilide. Yield 85%, m.p. 74°C. ^{1}H NMR ($CDCl_3$, 200 MHz: δ) 0.89 (t, J=6.8 Hz, 3H), 1.24–1.84 (m, 12H), 2.27 (s, 1H), 3.98 (t, J=6.6 Hz, 2H), 7.22 (dd, J=2.9, 9.3 Hz, 1H), 7.65 (d, J=2.9 Hz, 1H), 8.62 (d, J=9.3 Hz, 1H), 10.06 (s, 1H).

For 2-nitro-4-decyloxyacetanilide: yield 83%, m.p. 77°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.89 (t, J=6.8 Hz, 3H), 1.24–1.83 (m, 16H), 2.27 (s, 1H), 3.98 (t, J=6.6 Hz, 2H), 7.22 (dd, J=2.9, 9.3 Hz, 1H), 7.64 (d, J=2.9 Hz, 1H), 8.62 (d, J=9.3 Hz, 1H), 10.06 (s, 1H).

2-Nitro-4-alkoxyanilines.

These compounds were obtained by hydrolysis of the respective 2-nitro-4-alkoxyacetanilides in HCl (*10*). The product, which precipitated from the reaction mixture after dilution with water, was dried and then crystallised from hexane. The yield was 90% for both obtained compounds.

For 2-nitro-4-octyloxyaniline: m.p. 58°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.89 (t, J=6.8 Hz, 3H), 1.23–1.80 (m, 12H), 3.92 (t, J=6.6 Hz, 2H), 5.88 (s, 2H), 6.75 (d, J=9.3 Hz, 1H), 7.07 (dd, J=2.9, 9.3 Hz, 1H), 7.54 (d, J=2.9 Hz, 1H).

For 2-nitro-4-decyloxyaniline: m.p. 59°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.89 (t, J=6.8 Hz, 3H), 1.23–1.80 (m, 16H), 3.92 (t, J=6.6 Hz, 2H), 5.90 (s, 2H), 6.75 (d, J=9.3 Hz, 1H), 7.07 (dd, J=2.9, 9.3 Hz, 1H), 7.53 (d, J=2.9 Hz, 1H).

4-Alkoxy-1,2-diaminobenzenes.

The appropriate 2-nitro-4-alkoxyaniline was reduced with $SnCl_2$ in concentrated HCl, according to method proposed for 2-nitro-4-butoxyaniline (*11*). However, isopropanol was added to the reaction mixture in the same volume as HCl solution. After the reaction the isopropanol and HCl were evaporated to dryness under the vacuum. The residue was dissolved in water and alkalised with concentrated NaOH. The product was extracted with Et_2O, dried with anhydrous K_2CO_3 and crystallised with hexane. The yield was 60% for both target compounds.

For 4-octyloxy-1,2-diaminobenzene (**C8**): ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.88 (t, J=6.8 Hz, 3H), 1.22–1.76 (m, 12H), 3.24 (wide signal, 4H), 3.85 (t, J=6.5Hz, 2H), 6.25 (dd, J=2.9, 8.3 Hz, 1H), 6.31 (d, J=2.9 Hz, 1H), 6.61 (d, J=8.3 Hz, 1H). Mass spectroscopy: m/z=237.3 [M+H+]. Elemental analysis: calculated for $C_{14}H_{24}N_2O$, C 71.13%, H 10.25%, N 11.85%; found, C 71.08%, H 10.28%, N 11.87%.

For 4-decyloxy-1,2-diaminobenzene (**C10**): ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.88 (t, J=7.1 Hz, 3H), 1.22–1.76 (m, 16H), 3.26 (wide signal, 4H), 3.85 (t, J=6.6 Hz, 2H), 6.25 (dd, J=2.9, 8.3 Hz, 1H), 6.31 (d, J=2.9 Hz, 1H), 6.61 (d, J=8.3 Hz, 1H). Mass spectroscopy: m/z=265.3 [M+H+]. Elemental analysis: calculated for $C_{16}H_{28}N_2O$, C 72.66%, H 10.69%, N 10.60%; found, C 72.64%, H 10.67%, N 10.60%.

3. Results and discussion

Here we present new, simple, diamino derivatives with a one-ring mesogenic core (Figure 1 a) having two donor–acceptor sites able to create multiple hydrogen bonds between the molecules.

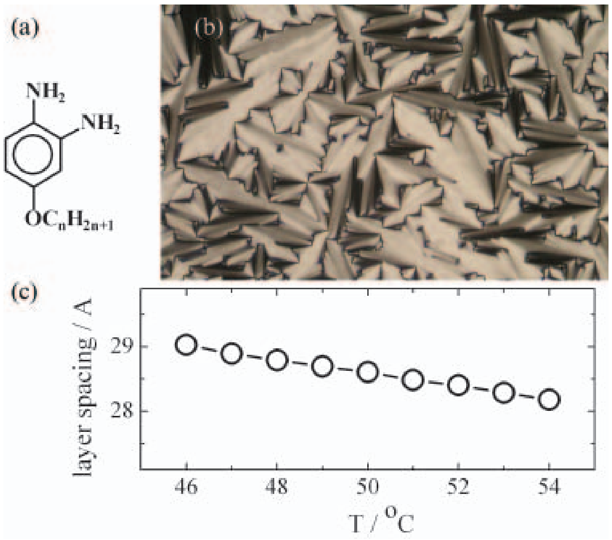

Figure 1. (a) Chemical structure of studied compounds for **C8** (n=8) and **C10** (n=10). (b) Optical texture of SmA phase formed by binary mixture of studied compounds, **Mix1**. (c) Temperature evolution of layer spacing in SmA phase of **Mix1**, obtained from X-ray diffraction.

Both homologues studied, **C8** and **C10**, exhibit a smectic A (SmA) phase (Table 1).

The mesophase was identified from its fan texture in the planar samples (Figure 1 b), typical for smectic phases, and the homeotropic texture in the one-surface-free samples, typical for the orthogonal phases. Calorimetric and optical studies showed the monotropic nature of the SmA phase (Figure 2 a). However, in an equimolar mixture of the two homologues, **Mix1**, the crystalline phase stability is significantly suppressed and an enatiotropic SmA phase is easily observed (Figure 2 b).

The clearing temperatures of the studied compounds, T_c~50°C, are much lower than those of well known one-ring mesogens that form dimers, e.g. 4-alkoxybenzoic acids (*7*) of similar molecular length (T_c~150°C), which indicates much weaker interaction between the molecules.

Optical observations show that the smectic phases of the studied materials have unusually low birefringence, Δn~0.03 (Figure 3).

Table 1. Phase sequence of studied materials. Phase transition temperatures are given in °C and enthalpy changes (in parentheses) in J g^{-1}. **Mix1** is an equimolar mixture of **C8** and **C10** materials.

Material	Phase transtions
C8	Cr 54.8 (86.4) [SmA 50.8 (6.1)] I
C10	Cr 63.9 (140.4) [SmA 57.6 (4.8)] I
Mix1	Cr 51.1 (75.4) SmA 54.2 (6.7) I

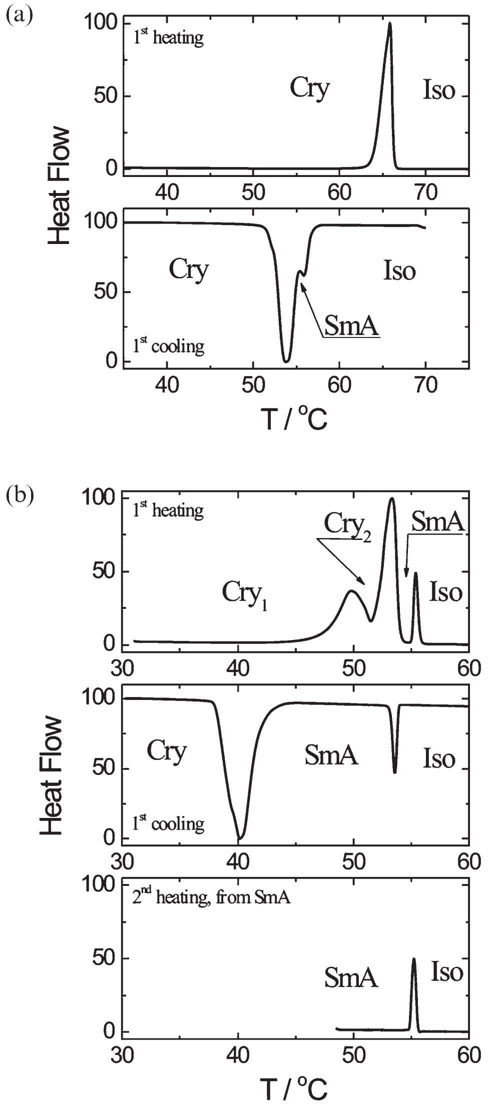

Figure 2. DSC thermograms for (a) compound **C10** and (b) binary mixture of **C8** and **C10** (**Mix1**). Note that whereas in the pure compound **C10** the SmA phase is monotropic, it becomes enantiotropic in binary mixture **Mix1** due to destabilization of crystalline phase.

For comparison, Δn measured at T_c-T=4 K for 4-pentylkoxybenzoic acid (**5OBA**) in the nematic phase is about 0.24 and for the two-ring mesogen, n-pentyl-4′-n-pentanoyloxybiphenyl-4-carboxylate [**54COOBC** (*12*)] in the SmA phase is about 0.18. Since the optical birefringence reflects the anisotropy of electric polarizability of the molecules (*13*, *14*), which is related to the shape of molecules, we conclude that for the studied compounds molecular dimers are not formed, since this would lead to significantly higher anisotropy. The relative anisotropy of polarizability can be derived form Vuks equation (*13*),

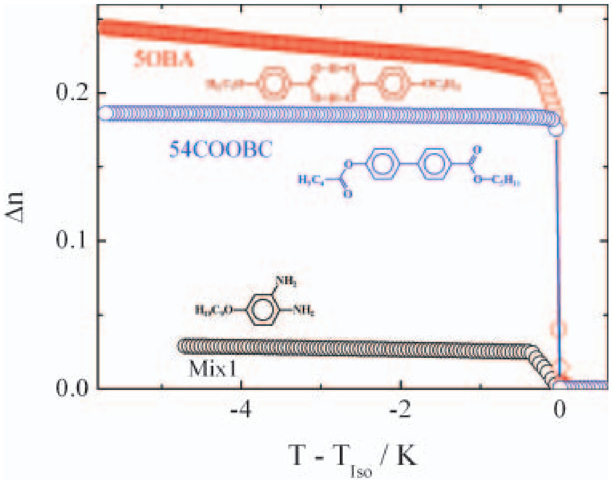

Figure 3. Temperature dependence of the optical birefringence at a wavelength 633 nm for **Mix1** (black). For comparison, results obtained at the same conditions for *n*-pentyl 4′-*n*-pentanoyloxybiphenyl-4-carboxylate (**54COOBC**, blue) and 4-pentyloxybenzoic acid (**5OBA**, red) are also given. Weak birefringence of studied diamino material points to very small shape anisotropy of the molecules. Estimated ratio of molecular polarizability along and perpendicular to long molecular axis does not exceed 1.1.

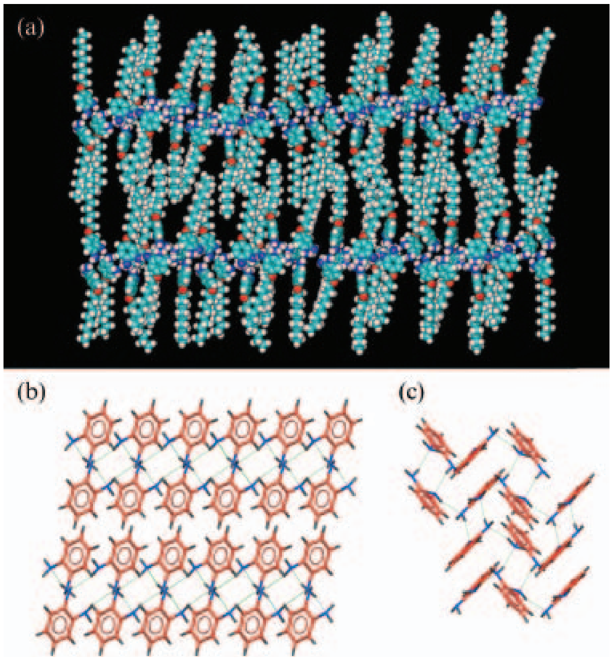

Figure 4. (a) Schematic model of molecular organization in SmA phase of diamino compound. Lamellar structure is imposed by network of hydrogen bonds connecting amino functional groups. (b, c) Two projections of crystal structure of parent non-mesogenic 1,2-diaminobenzene. Clearly visible are the layered structure (b) and network of hydrogen bonds built of 10- and 18-member rings (c).

$$\frac{\Delta\alpha}{\alpha}=\frac{2n\Delta n}{(n^2-1)S}, \qquad (1)$$

where $\Delta\alpha$ is the difference between molecular polarizability along and perpendicular to long molecular axis, α is the mean polarizability and S in the orientational order parameter,. Taking an S value between 0.6 and 0.9, which is rather typical for a smectic phase, a relative anisotropy of polarizability ranging from 0.12 to 0.08 is obtained for **Mix1**. This is significantly lower than for **54COOBC**, for which $\frac{\Delta\alpha}{\alpha}$ ranges from 0.72 to 0.48 assuming the same values for orientational order parameter. For **5OBA** the relative anisotropy of polarizability greater than 1 is obtained, even taking $S=0.5$, which is quite a high value for a nematic phase. In comparison, in lyotropic systems where the optical anisotropy is related exclusively to the order of alkyl chains, $\frac{\Delta\alpha}{\alpha}=0.012$ has been measured (*15*). One can conclude that for the studied materials the smectic layers are made of amine functional groups, interconnected by a two-dimensional (2D) structure of hydrogen bonds (Figure 4 a).

Layers, of almost zero anisotropy, are intersected by weakly anisotropic layers formed by phenyl rings and alkyl chains. The proposed structure is in agreement with the crystal structure of the parent, non-substituted diamino molecule (*16*). Diaminobenzene is not mesogenic and crystallises with a $P2_1/c$ space group. The crystal structure clearly indicates layer formation (Figure 4 b) in which a hydrogen bonded network is formed between the amino groups. The network of hydrogen bonds contains interconnected 10- and 18-atom rings (Figure 4 c). It can be expected that a similar network of hydrogen bonds, although with only short-range order, also exists in the smectic phase of the studied compounds. X-ray studies confirmed short-range in-layer order for the SmA phase of **Mix1**. Moreover, the X-ray measurements show that the layer spacing in the SmA phase (Figure 1 c), $d\sim 28.5$ Å, is about 1.5 times the molecular length obtained from modelling. This points to quite strong interdigitation of the molecule tails between the neighbouring smectic layers (Figure 4 a).

It is also worth noting that if the amine groups are exchanged for hydroxy groups, the compounds, 4-alkoxy-1,2-dihydroxybenzenes (*17*), lose their mesogenic properties. Comparing the crystalline structure of the parent compounds, 1,2-diaminobenzene and 1,2-dihydroxybenzene (*18*), it can be seen that both form a similar network of hydrogen bonds consisting of 10- and 18-member rings. However, there is a subtle difference in the relative orientation of benzene rings with respect to the layer defined by the network of hydrogen bonds. One can argue that an alkyl chain attached to the benzene ring in position 4 would be strongly inclined from the layer normal in the case of the dihydroxybenzene structure, which discourages formation of a smectic phase.

In summary, new compounds with simple molecular structure have been synthesized and shown to form a smectic phase. Lamellar structure is obtained through a 2D network of hydrogen bonds connecting amine groups. The reported phase structure is probably similar to that formed by simple carbohydrates (*19*); however, multiple hydroxy groups in carbohydrate molecules should lead to a more complex network of hydrogen bonds.

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