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Benzylidenehydrazine based room temperature columnar liquid crystals[†]

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We report on the synthesis and investigation of self-assembly properties of new benzylidenehydrazine based compounds, namely *N*-(2,3,4-tridodecyloxybenzylidene)-3,4,5-*N'*-trialkoxybenzoylhydrazines. They were confirmed to exhibit wide ranges of room temperature hexagonal columnar liquid crystalline phases (Col_h) as evidenced by optical polarizing microscope (OPM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) studies. Helical organization was confirmed for the Col_h* phase of a compound with chiral tails. More generally, combining the 2,3,4- and 3,4,5-substitution patterns of aromatic cores in one molecule provides a new way to low melting columnar LC materials with wide phase ranges.

Introduction

Supramolecular chemistry enables development of highly complex chemical structures from discrete components through non-covalent intermolecular forces. The materials obtained from it have been proved as potential candidates in the fields of life science and material science.¹ Especially liquid crystals (LCs) represent an exciting area of intense research² because of the self-assembly and self-healing ability, leading to the potential for applications in solar cells,3 ion-conducting materials for batteries,⁴ and other functional nanostructured materials. Among the non-covalent interactions, hydrogen bonding is one of the most important interactions because of its strength, directionality, reversibility and selectivity.5,6 The use of hydrogen bonding to form liquid crystalline (LC) materials,^{2a} in particular, discotic LC,⁷ is regarded as promising to develop functional materials. Hydrogen bonding between amides has been used to produce supramolecular columnar LC phases with simple benzamides,8 dibenzoylhydrazines9 and aryl substituted ureas10 as well as with multiple amide substituted aromatics.^{11,12} Chiral superstructures¹³ as well as polar order^{10,11c,e} were observed in columnar phases connected through hydrogen bonding via amide or urea groups.¹⁴ A major disadvantage of amide based mesogenic materials is the often observed relatively high melting temperature.8-11 In order to obtain low melting columnar LC materials we used an approach combining reduction of the number of hydrogen bondings by using the benzoylhydrazine unit with an uncommon 2,3,4-substitution pattern of the alkyloxy chains attached to the aromatic core.15 Though this

substitution pattern is readily available from 2,3,4-trihydroxybenzaldehyde its use was limited mainly to polycatenar LC molecules in order to replace smectic and columnar phases by nematic phases, especially in the search for biaxial nematic materials^{16,17} and for unusual dimesogens in the search for new mesophases.¹⁸ Beside the polycatenar compounds there is also one example of a hydrogen bonded mesogen based on this unit in a β -C-glycoside.¹⁹ Simple benzamides and dibenzoylhydrazines with the 2,3,4-substitution pattern do not form LC phases.⁶ To the best of our knowledge there is only a short note in a review⁶ where it is mentioned that *N*-[3,4,5-tridecyloxybenzoyl]-*N*'-2,3,4tridecyloxybenzylidenehydrazine forms a rather stable Col_h phase with a clearing temperature at 163 °C, but without giving any further details.

Herein we report a series of six-chain benzylidene hydrazides 1–5 combining two distinct benzene rings, one with a 2,3,4- and the other one with a 3,4,5-substitution pattern, having different chain lengths at the 3,4,5-substituted ring, and it is shown that all these material form broad regions of hexagonal columnar phases with melting points below room temperature for the shorter homologues. Moreover, a room temperature Col_h^* phase with helical superstructure was observed for compound **6*** with chiral tails.

Result and discussion

For the synthesis, 2,3,4-tridodecyloxybenzaldeyde was condensed with different 3,4,5-trialkoxybenzoylhydrazides to yield the target compounds **1–5** and **6*** in good yields (Scheme 1). The experimental procedures, the synthesis of the intermediates and analytical data are described in the ESI⁺.

The thermal behaviour of the compounds 1–5 and 6* was evaluated by polarizing microscopy, DSC and XRD studies (see Table 1). Compounds 1–3 and 6* turned out to be room temperature LCs. When placed between two glass slides, they can easily be sheared and show birefringent textures, clearly

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Scheme 1 Compounds 1–5 and 6* and their synthesis.

indicating that the materials are already in the liquid crystalline state at room temperature. This is confirmed by the DSC investigations with compounds 2 and 3 where transitions with relatively high enthalpy values (20-26 kJ mol⁻¹), assigned to melting/crystallization or transitions between the LC phases and crystalline mesophases, reproducibly occur in the heating and cooling traces at temperatures below 10 °C (Fig. 1a). No crystallization could be observed even after one year of storage at 20 °C which makes it unlikely that there are additional higher melting crystalline phases. Peaks in the DSC curves at higher temperature (around 162-166 °C for compounds 1-4; at 136 and 152 °C for compounds 5 and 6*, respectively) with enthalpy values between 5.2 and 10.8 kJ mol⁻¹ indicate the columnarisotropic transitions. For compounds 1-5 with linear chains there is an increase in clearing temperatures upon reducing the chain length, associated with a decrease of the melting temperatures, leading to the largest mesomorphic region for compound 1 with the shortest (C₉) chains. Only for the long chain compounds 4 and 5 the melting points are above room temperature.

Between crossed polarizers all compounds show textural patterns consisting of mainly pseudo-focal conic fan-shaped growth patterns with homeotropic regions appearing completely dark as shown in Fig. 2a and b (see also Fig. S2, ESI†). This indicates optically uniaxial columnar phases. On further cooling



Fig. 1 DSC traces obtained during the first heating/cooling cycles (10 K min^{-1}) of (a) compound 2 and (b) compound 6*.

the texture remains unaltered till room temperature; hence it seems that no additional phase transition takes place in the whole scanned temperature range, as also confirmed by DSC and XRD.

Compounds 1, 3 and 6* were investigated by XRD of aligned samples. In the wide-angle region there is a diffuse scattering with a maximum corresponding to d = 0.45-0.47 nm (Fig. 3 and S1, ESI†), which indicates the fluid character of the mesophases.

Table 1 Phase transition temperatures^{*a*} (°C) and enthalpies [kJ mol⁻¹] of the investigated N-(2,3,4-tridodecyloxybenzylidene)-N'-(3,4,5-trialkoxybenzyl)hydrazines



Compd.	R	Phase sequence			
		Heating	Cooling	<i>a</i> _{hex} /nm	n _{cell}
1	C ₉ H ₁₉	M -12 [2.6] Col _b 166 [8.4] I	I 160 $[-7.4]$ Col _b ^b	2.62-2.64	1.3
2	$C_{10}H_{21}$	$Cr - 2 [23.6] Col_h 162 [5.6] I$	I 158 $[-5.2]$ Col _h -12 $[-20.3]$ Cr		
3	$C_{11}H_{23}$	Cr 3 [26.1] Col _h 163 [7.6] I	I 156 [-6.8] Col _h -7 [-25.7] Cr	2.73-2.75	1.3
4	$C_{12}H_{25}$	Cr 66 [49.5] Col _h 162 [7.1] I	I 156 [-6.5] Col _h -2 [-41.3] Cr		
5	$C_{16}H_{33}$	Cr 56 [98.3] Col _h 136 [5.2] I	I 132 [-4.9] Col _h 26 [-51.7] Cr		
6*	(S)-3,7-dimethyl-octyl	Col _h * 152 [10.8] I	I 145 $[-9.4]$ Col _h * ^c	2.63-2.67	1.3

^{*a*} Peak temperatures in the DSC thermograms obtained during the first heating/cooling cycles at 10 K min⁻¹; abbreviations: Cr = crystalline solid state, $Col_h = hexagonal$ columnar phase, $Col_h^* = hexagonal$ columnar phase with chiral superstructure, M = unknown crystalline/LC phase, I = isotropic liquid state. ^{*b*} No crystallization peak was observed down to -20 °C. ^{*c*} No melting/crystallization peak was observed in DSC plots (down to -20 °C).



Fig. 2 Microphotographs of the optical textures (crossed polarizers) obtained for Col_h phases of (a) compound 4 at 151 °C (dark areas represent homeotropically aligned regions), (b) compound 1 at 160 °C, and (c) same region with λ -retarder plate; the indicatrix orientation in the compensator and in the two types of fans is shown in the inset.

Only a single reflex was observed in the small angle region of the powder patterns of all compounds. In the 2D diffraction patterns of aligned samples the diffuse scattering has a ring-like shape and the small angle scattering splits off into a hexagonal pattern (Fig. 3 and S1, ESI†) confirming a hexagonal lattice with $a_{hex} = 2.6-2.7$ nm (see Tables 1 and S1, ESI†). The number of molecules per unit cell with a hypothetical height of *h*, corresponding to the *d*-value of the maximum of the diffuse wide angle scattering, is about $n_{cell} = 1.3$ for all investigated compounds (see Tables 1 and S2, ESI†). This indicates that the columns are essentially formed by only one molecule in the cross-section, but with a significant staggering and overlapping of the molecules along the column long axis. The lattice parameter a_{hex} slightly decreases with increasing temperature (Table S1, ESI†), as usually observed for



Fig. 3 (a) X-Ray diffraction pattern of an aligned sample of the Col_h phase of compound 1 at 155 °C, and (b) θ -scan of the diffraction pattern.

columnar phases, due to increased folding of the alkyl chains at higher temperature.^{17,20}

The columnar phases are optically negative as indicated by the colours of the fans observed with an additional λ -retarder plate (Fig. 2c). This means that the main π -conjugation pathway is perpendicular to the column long axis, which indicates that the aromatic units of the molecules should be arranged predominately perpendicular to the column long axis as shown in the model in Fig. 5b.²¹

IR investigation of the bulk samples at room temperature reveals the presence of N–H stretching vibrations (ν_{N-H}) at 3225 cm⁻¹ and $\nu_{C=O}$ at 1638 cm⁻¹ confirming hydrogen bonding through N–H…O=C along the columns.²² The disordered state of the alkyl chains is additionally confirmed by the positions of symmetric and asymmetric C–H stretching at 2918 cm⁻¹ and 2850 cm⁻¹, respectively.^{9b,22}

Based on these investigations the formation of columnar LC phases is the result of nanosegregation^{8c,23} of the polar benzylidenebenzoylhydrazine cores in columns. These columns are enclosed by the fluid alkyl chains forming a non-polar continuum around them (see Fig. 5). In the middle of the columns cooperative hydrogen bonding²⁴ between the N–H and C=O groups of adjacent molecules form chains which interconnect the molecules along the column long axis and in this way stabilize the columnar aggregates.^{8,22} As hydrogen bonding along the columns requires a uniform orientation of the C=O dipole moments more or less



Fig. 4 CD spectra obtained in the columnar phase of compound 6* as a function of temperature.

parallel to the column long axis there is the possibility of polar order along these columns. For this reason compound 1 was investigated under low frequency AC triangular wave electric field (ITO coated cell, 10 µm) which was increased gradually. Even for high voltages (200 Vpp), no switching was observed, indicating the absence of polar order in the columnar structure. It seems that the presence of only one proton donor group in each molecule is not strong enough to create sufficiently long strings with uniform direction of the C=O groups to provide ferroelectric or antiferroelectric switching of these columnar phases, as observed for ureas¹⁰ and bisamides,^{11e} having additional hydrogen bonding donor sites. Probably, in compounds 1-5 and 6* hydrogen bonding with other proton acceptor groups (imine-N, ether-O) or the contribution of cyclic dimeric aggregates could interrupt the polymeric N-H···O=C hydrogen bonding chains. This distortion of polymeric hydrogen bonding also contributes to lower transition temperatures observed for the benzoylhydrazones compared to related diacylhydrazides and ureas.

As indicated by the negative birefringence the aromatic cores are arranged on average perpendicular to the columns. In order to organize on a hexagonal lattice in which the columns posses on an average circular cross-section, there must be a time and space averaging of the orientation of the elliptical molecules along the column long axes. One possible way to achieve this is by formation of a helical superstructure along the column long axis (Fig. 5b) where the N–H \cdots O=C hydrogen bonding chains adopt a helical conformation¹⁴ and the benzoylbenzylidenehydrazine cores are twisted with respect to each other by a distinct angle in a uniform sense. In order to check this possibility the chiral compound 6* having branched chiral tails with (S)-configuration of the stereogenic centres was synthesized. Microscopic and DSC investigations indicate a wide range of columnar mesophase (Col_h*) on heating and having no signature of any melting peak above a temperature of -20 °C. A similar kind of thermal behaviour was observed on cooling (Fig. 1b). Molecular chirality induced handedness in the macroscopic fluid columnar structure was probed by Circular Dichroism (CD) spectroscopic study. For this purpose, a thin film of neat sample was prepared using quartz plates and spectra were recorded as a function of



Fig. 5 Schematic representation of columns in which molecules of compound 6^* self-assemble in a helical organization.²¹

temperature from its isotropic phase. The columnar phase of compound 6^* exhibits a strong cotton effect which occurs at the transition from the isotropic liquid state to the columnar phase, confirming a helical superstructure in the columnar phase (Fig. 4). A possible model of the organization of the molecules in the columns of compound 6^* is shown in Fig. 5. However, it must be considered that the model was simplified, as in fact there is some additional staggering of the molecules within the columns, which could provide a more improved space filling in the periphery of the molecules than actually shown in Fig. 5b.

Conclusions

We have demonstrated the formation of thermally stable, wide range room temperature columnar liquid crystals by combining 2,3,4- and 3,4,5-trisubstituted aromatics in benzoylated benzylidene hydrazines, which make them advantageous with respect to other hydrogen bonding amide based liquid crystals (hydrazides, amides and ureas). It seems that the distorting effect of the 2,3,4-substitution pattern, together with the limited number of H-donor groups available for intermolecular hydrogen bonding interactions, are responsible for the low melting temperatures whereas the 3,4,5-substituted unit provides a sufficiently high stability of the columnar LC phases. The phase range is considerably widened by reducing the chain length, mainly due to the reduction of the melting points. However, it seems that the reduced number of hydrogen bonding sites does not allow the formation of polar order along the column axis as observed for some columnar LC based on ureas.¹⁰ The occurrence of a strong CD signal (compound **6***) indicates a chirality induced helical organization of the molecules within the columnar structure stabilized through hydrogen bonding. More generally, it is suggested that the concept of combining of 2,3,4- and 3,4,5-substituted aromatics at the periphery of larger disc-like π -conjugated molecules could provide an additional way to obtain low melting columnar LC materials with wide phase ranges for molecular electronics applications.²⁵ This concept needs to be further explored in the future.

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