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Modifications of the mesophase formation of discotic triphenylene compounds by substituents

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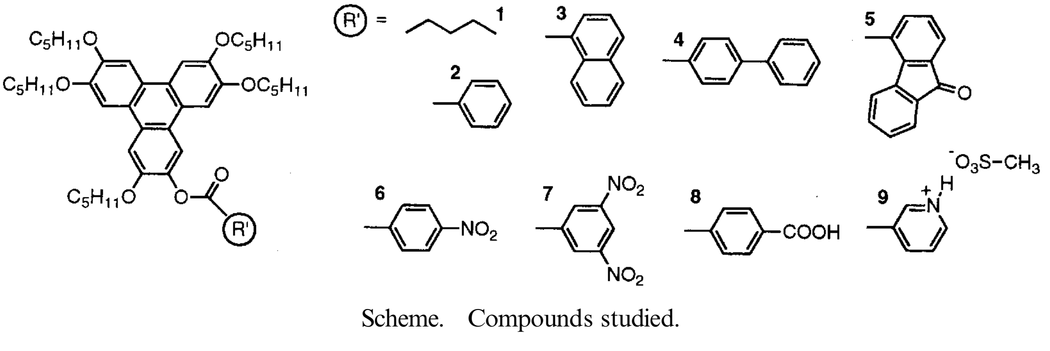
Columnar discotic carboxylic esters of 2-hydroxy-3,6,7,10,11-penta(1-pentyloxy)triphenylene, characterized by a variety of functional groups, were prepared with the purpose of studying the effects of the substituents on the mesophase behaviour. Bulky substituents and polar substituents were found to destabilize the columnar mesophase. The clearing temperature is lowered and the melting point of the crystalline phase, as well as the tendency to crystallize from the mesophase, is increased. Specific substituents cause the formation of novel discotic mesophases characterized by a superstructure.

1. Introduction

Disc-shaped molecules have the tendency to form columnar mesophases in which the mesogens are stacked closely and regularly within columns [1–4]. Such columns are characterized by a rapid unidirectional transport of excitations or charge carriers [5–10]. This makes such materials interesting candidates for applications in the area of opto-electronics [5–12]. For instance, examples considered have been applications as photoconductors [8–10] or as charge carrier material in organic light-emitting diodes [11, 12].

The majority of investigations in this area are limited to hexa-*n*-alkoxytriphenylenes, yet these compounds have a tendency to become polycrystalline at room temperature and the columnar phases are only stable at elevated temperatures [2, 13]. Crystallization can be strongly suppressed by replacing one of the alkoxy groups by an alkanoyloxy group [14] (see the scheme). This approach opens up a diversity of routes towards functionalized triphenylene compounds via an appropriate variation of the chemical nature of the substituent. We have shown recently that a highly ordered columnar phase—a plastic columnar phase—may be induced in this way and the same holds for the induction of reentrant behaviour involving columnar discotic phases [3, 15]. The investigatons have revealed that such structural variations are also connected with an increase of the glass transitions [16], which allows one to obtain stable, highly ordered films at room temperature, and also with variations of the opto-electronic properties. It therefore seems worthwhile to explore various types of substituents carrying different functions.

It is, however, obvious that such substitution will not stabilize the columnar phases or even enhance their order in all cases. Chromophore units which are bulky and which by themselves are not mesogenic can be



Scheme. Compounds studied.

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envisioned as destabilizing columnar phases. The same may be true for substituents carrying strong dipole moments, even though the direct substitution of dipolar groups into the discogen ring has been reported to enhance the range of the mesophase [17]. Lateral modifications of the chemical structure will in any case very strongly disturb the sixfold rotational symmetry, which is of benefit for the formation of hexagonal columnar phases. We may therefore expect modified transition temperatures, but also possibly new structural features which, in turn, may correlate with novel electronic properties. This contribution considers therefore the effect of large aromatic substituents and of substituents carrying strong dipole moments on the thermodynamic properties and structure formation.

Table 1. Melting temperatures T_m of the crystalline phase and clearing temperatures T_i of the mesophase, as well as clearing enthalpy ΔH_i and entropy ΔS_i. n.d.: transition could not be detected. Melting enthalpies and entropies are not given as they depend strongly on the degree of crystallinity. ( ) indicates a monotropic transition.

Compound	T_m/°C	T_i/°C	ΔH_i/J g^{-1}	ΔS_i/J g^{-1} K^{-1}
1	47	178	23.9	0.053
2	n.d.	193	26.0	0.056
3	103	158	8.7	0.020
4	94	135	5.3	0.013
5	147	(124)	8.9	0.022
6	74	190	18.6	0.040
7	131	201	8.0	0.017
8	203	n.d.	n.d.	n.d.
9	199	(168)	11.0	0.025

2. Experimental

The compounds studied are represented in the scheme. Compound **1** has already been described in the literature [14] and is used as a reference compound, **2** is a compound with an aromatic substituent of similar size. Compared with compound **2**, compounds **3**–**5** have aromatic substituents with increasing size and **6**–**9** are strongly polar compounds. The compounds shown in the scheme were prepared by esterifying 2-hydroxy-3,6,7,10,11-penta(1-pentyloxy)triphenylene [18, 19] with acid chloride as described previously [3]. For purification, the compounds were recrystallized from ethanol. They were obtained as crystalline or partially crystalline materials.

The temperatures and enthalpies of the phase transitions were determined by differential scanning calorimetry (Mettler DSC 30) at a heating rate of 10 K min^{-1}. The second heating run was used for the evaluation of the clearing transitions and the transitions between mesophases. The melting behaviour was characterized from the first heating run of the recrystallized sample.

Structures were analysed by wide angle X-ray scattering (WAXS). A goniometer (Siemens D5000) was employed in the $\Theta/2\Theta$ mode. Ni-filtered CuK$_\alpha$ radiation was used in all cases. The temperature was controlled to within 1 K.

3. Results and discussion

3.1. *Thermodynamic properties*

DSC investigations were performed to obtain the melting and transition temperatures from the columnar phase to the isotropic phase; the table summarizes the phase transition temperatures. The columnar phase was in all cases a hexagonal columnar phase (see below). The melting temperatures of the crystalline phase and the clearing temperatures of the liquid crystalline phase are plotted in figure 1 for substituents of different sizes. It is obvious that the columnar phase is increasingly destabilized for compounds with aromatic substituents of increasing size. The clearing temperature is decreased from 193 to 124°C and the clearing enthalpy and entropy are decreased, as well. The mesophase is also destabilized with respect to the crystalline phase, as is obvious from the increase of the crystal melting temperature from 47 to 147°C. In the case of the fluorenyl compound **5**, only a monotropic mesophase can be observed. The tendency towards crystallization is also increased for the larger substituents. While compound **2** shows no crystallization and compound **1** crystallizes from solution only, we observe that **3**–**5** show crystallization from the melt. Compounds **3** and **4** crystallize after annealing for 10 min at 20 K below the melting temperature. Compound **5** even shows partial crystallization during DSC measurements at a cooling rate of 10 K min^{-1}.

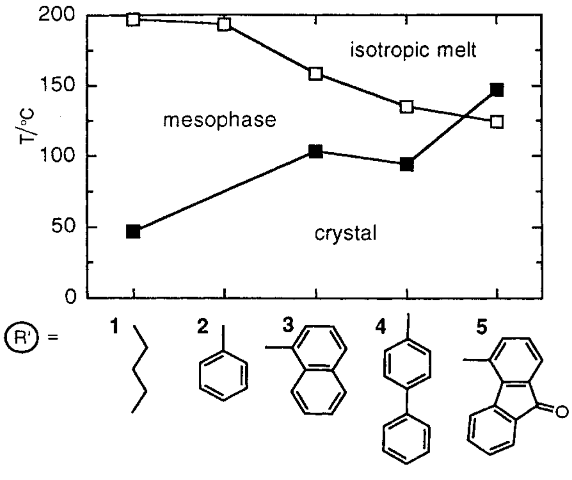

Figure 1. Melting and clearing temperatures for compounds with substituents of different size and polarity.

For the strongly polar compounds **6**–**9**, a different behaviour was observed. The polar substituents did not lead to a significant decrease of the clearing temperature. A clearing temperature below that of the reference compound **1** was observed only for the salt **9**; clearing enthalpies and entropies, however, were significantly decreased. In contrast, the melting point is strongly affected by polar substituents. The mononitro compound **6** already shows a higher melting point than the reference compound **1**. For the dinitro compound **7**, the melting point is raised to 131°C and for the terephthalic acid ester **8** and the salt **9** the melting point is near 200°C. Thus, of these polar compounds, only **6** and **7** show a thermodynamically stable mesophase. No mesophase is observed for **8** and only a monotropic mesophase is observed for **9**. The tendency towards crystallization also increases strongly for the more polar compounds. While **6** crystallizes after storing at room temperature for a month, **7**–**9** crystallize rapidly. Compound **9** can be supercooled into a glassy state by cooling at a rate faster than 30 K min^{-1}. For **7** and **8**, the crystallization process cannot be significantly supercooled.

3.2. *Structure*

The variation of the substituent affects not only the phase transition temperature, but also the structure of the columnar phases. All the liquid crystalline compounds exhibit a columnar hexagonal ordered phase Col$_{\text{ho}}$ [2, 13], where the molecules are stacked to form columns and these columns are arranged on a two dimensional hexagonal lattice with a hexagonal lattice constant a_{hex} of approximately 20.0 Å. Yet some of the compounds reveal additional structural features as became apparent from the X-ray diagrams.

Figure 2 shows the X-ray diffraction diagrams in the small angle region. Compound **2** shows the normal diagrams characteristic for the Col$_{\text{ho}}$ phase with only the (1 0 0) reflection in the small angle region. In comparison, the compounds with larger aromatic substituents, **3**–**5**, show an additional reflection near 2.7°, whereas no difference is observed for larger scattering angles. The additional peak corresponds to a *d*-spacing twice as large as that for the (1 0 0) reflections. Thus, this reflection must be due to a superstructure in the hexagonal lattice. The new unit cell has to have at least one lattice dimension that is twice as large as the intermolecular distance. We have therefore tentatively labelled the new reflection (1/2 0 0) in order to keep the labelling of the (1 0 0) reflection unchanged. It seems that the large aromatic substituents lead to the formation of a specific structure in the side group region. We assume that demixing between aromatic and aliphatic side chains is the driving force for this. Two possible models for the molecular arrangement are represented in figure 3. The superstructure can be realized if either two or three aromatic substituents each point towards each other within the hexagonal arrangement. However, this must not be regarded as a static structure. The rotational mobility of the molecules around the column axis, which is characteristic for the Col$_{\text{ho}}$ phase, will still continue. The structures shown in figure 3 should therefore be regarded as a preferred configuration. So far, compounds which show the superstructure over the entire mesophase range and compounds which do not show it at all have been found. No phase transition between a Col$_{\text{ho}}$ phase with superstructure and a Col$_{\text{ho}}$ phase without superstructure has been observed.

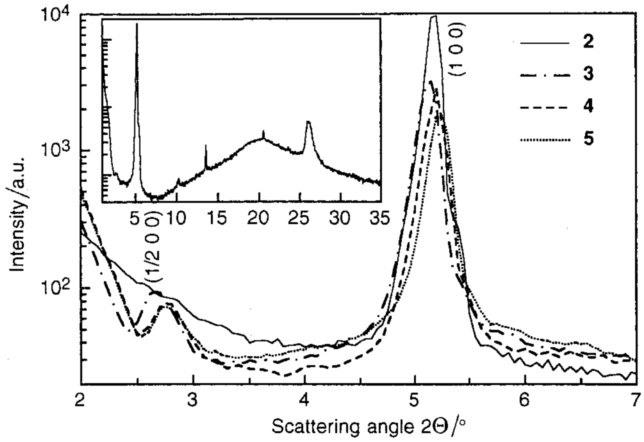

Figure 2. X-ray diffractograms for compounds **2**–**5** in the small angle region. The inset shows the diffraction diagram for compound **2** over a wider range of scattering angles. Except for the reflection near 2.5°, similar diffraction diagrams have been observed for all the compounds in the Col$_{\text{ho}}$ phase.

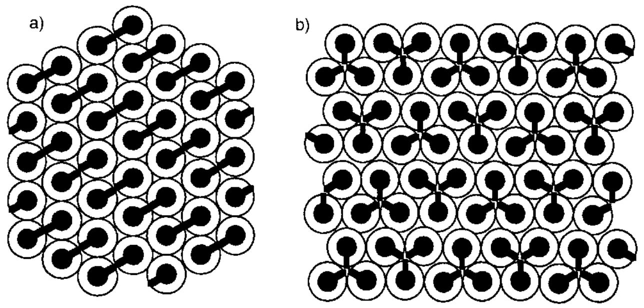

Figure 3. Possible models for the superstructure of the hexagonal lattice of compounds **3**–**5**. The aromatic core and the aromatic substituent are represented in black, and the aliphatic side chains in white. A configuration where (*a*) 2 or (*b*) 3 aromatic side groups point towards one another would give rise to the reflection observed in figure 2.

We found, however, that the biphenyl compound **4** not only forms the superstructure, but also shows a very interesting structural and phase formation behaviour. The DSC trace of this compound, figure 4 (*a*), shows two first order phase transitions at 113°C ($\Delta H = 4.7\,\mathrm{J\,g^{-1}}$) and 135°C, respectively. The X-ray traces for both phases are represented in figure 4 (*b*). The $\mathrm{Col_{ho}}$ phase is formed at lower temperatures, as indicated by the presence of the reflections (1 0 0), (1 1 0) and (0 0 1). This X-ray diagram does not change significantly up to 100°C. The diffraction diagrams at 120°C is very similar, yet it displays a peculiar feature with respect to the shape of the (1 0 0) reflection. While the upper part of the reflection remains sharp, the lower part becomes very broad. Such a peak shape results from strong thermal fluctuations on a two dimensional lattice [20]. While it is not surprising that such fluctuations occur at elevated temperatures, it was quite unexpected that a phase with these fluctuations is separated from a phase without these fluctuations by a first order phase transition. The large aromatic substituent apparently destabilizes the $\mathrm{Col_{ho}}$ phase and induces a less ordered columnar phase.

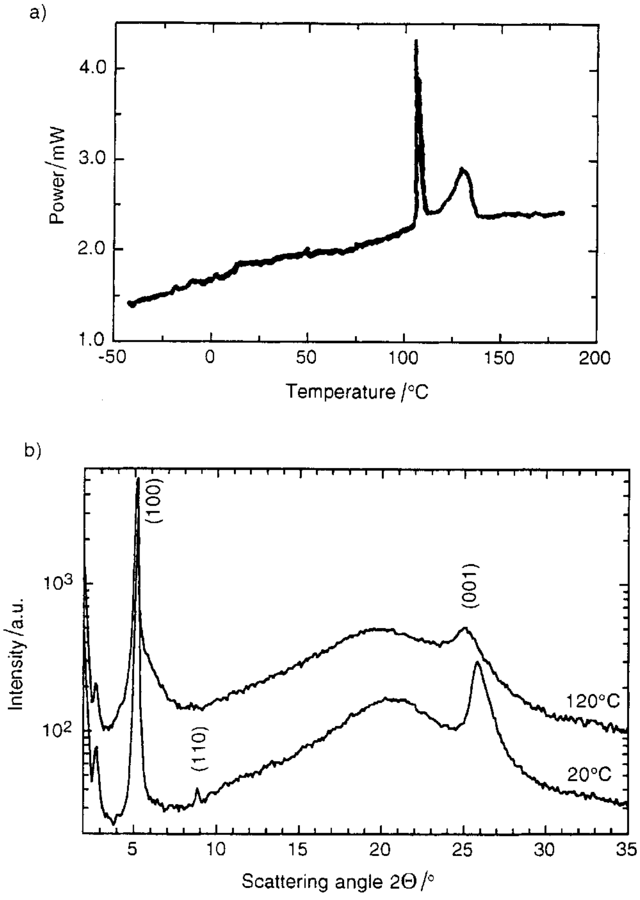

Figure 4. (*a*) DSC trace and (*b*) WAXS diagrams for compound **4** showing both mesophases.

4. Conclusion

The investigations have revealed that both the structure of columnar phases of discogens, as well as the stability of such phases, can be strongly modified for triphenylene compounds via the selection of substituents. The general tendency is that the mesophase is destabilized with respect to the crystalline state and in many cases with respect to the isotropic phase. This indicates that a functionalization of such compounds, for instance with chromophores or strongly polar groups, with the aim of keeping the columnar phase will be successful only if the substituents are carefully chosen. Another conclusion is that novel properties, in particular optoelectronic and transport properties, may result from such functionalizations due to a partial phase separation of such functional groups within the hexagonal structure combined with the formation of a superstructure.

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