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B. Glösen^a; W. Heitz^a; A. Kettner^a; J. H. Wendorff^a

^a Department of Physical Chemistry and Center of Material Science, Philipps-University, Marburg, Germany

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A plastic columnar discotic phase D_p

by B. GLÜSEN, W. HEITZ, A. KETTNER and J. H. WENDORFF*

Department of Physical Chemistry and Center of Material Science,
Philipps-University, 35032 Marburg, Germany

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A plastic columnar discotic phase is reported for an asymmetrically substituted triphenylene. It is characterized by a three-dimensional crystal-like registry of ordered columns in a hexagonal lattice while the disc molecules within the columns are able to rotate. At the phase transition from the normal discotic hexagonal phase to the new phase only very minute changes in structure and dynamics occur.

1. Introduction

The general observation for ordered discotic columnar phases is that the one-dimensional positional order along the axis of the column and the two-dimensional positional order defined by the packing of the columns are not correlated [1, 2]. This is obvious from the fact that no mixed reflections (hkl) are observed in X-ray measurements. This correlation is apparently destroyed by statistical shifts of the columns along their normal. The presence of mixed reflections (hkl) is usually taken as an indication that a crystalline state has been formed.

While calamitic mesogens are known to form several smectic mesophases with three-dimensional positional order [3], reports on corresponding phases for discotic mesogens are rare. It is known that hexasubstituted chloromethylbenzenes [4] form structures with a three-dimensional positional order and free rotation of the molecules around their axis. The formation of a typical liquid crystal structure with well-ordered areas formed by the cores and disordered areas formed by the side chains, is, however, not observed in this case, since the molecules are entirely rigid. Certain hexathiotriphenylenes [5] and tribenzylens [6] form phases with a three-dimensional positional order of the centres of the molecules and a helical order within the columns. Here, of course, the free rotation of the molecules on their sites cannot take place any more, because this would destroy the helical order. These substances are typical mesogens with a rigid core and a flexible peripheral part. Only the rigid cores are ordered as described above; the flexible side-chains exhibit a liquid-like structure.

This contribution is concerned with a novel discotic columnar phase which helps to fill the gap between ordered columnar phases and the crystalline state. In

contrast to the known helical phases the new phase is very closely related to the liquid crystalline phase. Besides the occurrence of three-dimensional positional order no major structural changes are observed and it displays relaxations including the glass relaxation similar to the ones observed for the hexagonal columnar phase. The novel phase has features in common with the plastic crystalline state and it is for this reason that we propose to call it plastic columnar discotic phase.

Highly ordered columnar phases are of considerable interest because of their high charge-carrier mobility in photoconductivity experiments [7]. Therefore the direct transition from the discotic hexagonal ordered phase to the discotic plastic phase, with only minor changes in structure and dynamics of the mesophase, may be especially useful in trying to understand the nature of the photoconductivity.

We report results on the asymmetrically substituted triphenylene 3,6,7,10,11-pentapentyloxytriphenylene-2-yl pivaloate (pivaloate). The synthesis is described below (see scheme 1).

2. Preparation of materials

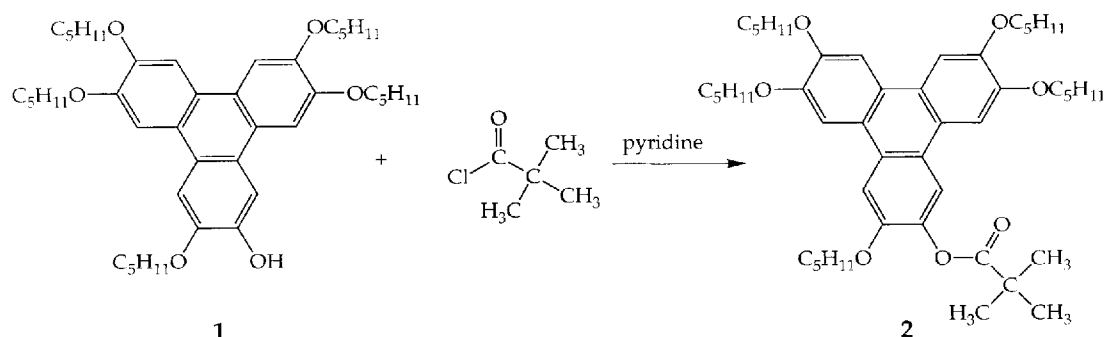
2.1. Synthesis of 1

2-Hydroxy-3,6,7,10,11-pentapentyloxytriphenylene was prepared as described elsewhere [8].

2.2. Synthesis of 2

To a solution of 673 mg (1 mmol) of **1** in 1 ml of pyridine, 181 mg (1.5 mmol) of pivaloyl chloride are added. The mixture is heated for 1 h at 80°C. Work-up is performed by dissolving the mixture in diethyl ether and washing the organic layer several times with dilute HCl and Na₂CO₃ solution. The crude product, isolated by evaporation of the organic layer, is purified by recrystallization from ethanol. Thus 548 mg (72 per cent) of **2** are isolated as a white sticky powder. ¹H NMR

* Author for correspondence.



Scheme 1.

(300 MHz, CDCl_3): $\delta = 8.00\text{--}7.76$ ppm (m, 6H, Ar-H), 4.30–4.18 ppm (m, 10H, Ar-CH₂), 2.00–1.82 ppm (m, 10H, ArCH₂CH₂), 1.60–1.40 ppm (m, 20H, Ar-CH₂CH₂(CH₂)₂), 1.46 ppm (s, 9H, C(CH₃)₃), 1.02–0.92 (m, 15H, Ar(CH₂)₄CH₃); ¹³C NMR (75 MHz, CDCl_3): $\delta = 172.0$ (C=O), 149.5, 149.4, 149.1, 148.9, 148.6, 139.8 (O-substituted C-atoms of triphenylene), 127.7, 124.5, 123.6, 123.1, 123.0, 120.8 (inner C-atoms of triphenylene), 116.5, 108.1, 107.2, 106.9, 106.8, 105.5 (H-substituted C-atoms of triphenylene), 69.8, 69.7, 69.3, 68.5 (Ar-CH₂), 39.0 (C(CH₃)₃), 29.0 (Ar-CH₂CH₂), 28.2 (Ar-CH₂CH₂CH₂), 27.3 (C(CH₃)₃), 22.4 (Ar-(CH₂)₃CH₂), 14.0 (Ar-(CH₂)₄CH₃).

3. Characterization techniques

The transition temperatures were determined by differential scanning calorimetry (Mettler DSC30) with a heating rate of 10 K min⁻¹. The structure was analysed using wide angle X-ray scattering (WAXS). The scattering curves were obtained using a Siemens D-5000 diffractometer; Ni-filtered CuK_α radiation was used in all cases. The temperature was controlled to within 1 K. Flat camera investigations were performed on samples oriented within glass capillaries.

The relaxation behaviour was analysed using dielectric relaxation spectroscopy covering a frequency range from 20 Hz–1 MHz (Hewlett-Packard impedance analyser HP 4284 A). A nitrogen gas heating system and the fully computer controlled measurement ensured a precision of 0.2 K within a temperature range of 100–470 K. The detailed set-up has been described previously [9]. The samples were prepared by melting into the isotropic state on gold covered electrodes made of stainless steel.

4. Results and discussions

The DSC diagram (figure 1) reveals the presence of three endothermic transitions on heating and a glass transition. The transition energy (in brackets) is high for the transition into the isotropic phase, indicating strong structural changes at this transition, and small for the

remaining transitions, thus indicating minor structural changes.

g -43°C ($\Delta C_p = 15 \text{ J}(\text{gK})^{-1}$)
 ? -5°C (0.5 kJ mol^{-1}) D_{hp} 65°C (0.4 kJ mol^{-1}) D_{ho}
 178°C (20.3 kJ mol^{-1}) I

We were not yet able to perform X-ray measurements below room temperature, so we could not examine the structure of the phase below -5°C . The X-ray diagram of the high temperature LC phase (see figure 2)† displays several Bragg peaks at smaller scattering angles which can be attributed to a two-dimensional hexagonal lattice with a lattice constant of $a_{\text{hex}} = 20 \text{ \AA}$ (see the table). The halo in the wide angle regime is caused by the amorphous packing of the alkyl chains and the broad asymmetric 'ordered' peak at 3.55 \AA marks the intracolumnar order. No mixed reflections (hkl) occur. This scattering diagram is thus characteristic for a D_{ho} phase [1, 2].

The calorimetrically detected transition into the lower temperature LC phase does not change the X-ray reflections observed in the small angle range, as is obvious from figure 2 and the table. The rather broad and asymmetric peak in the wide angle range, however, splits into two reflections and we observe the occurrence of an additional narrow reflection at intermediate scattering angles (see the table).

We performed flat camera investigations on oriented samples in order to obtain information on the origin of the additional reflections. The results are that the wide angle doublet has to correspond to (002) and (102) reflections and the intermediate reflection (at 4.7 \AA) to the mixed reflection peak (211), and not to the (310) reflection: the mixed peak displays four maxima with respect to the azimuthal intensity distribution.

In order to get more detailed information on the

†Note that a shoulder appears on the high angle side of the first reflection at low scattering angles. We have observed similar shoulders either on one or even on both sides for various discotic systems. We believe that such shoulders indicate the presence of distortions of a yet unknown nature [15].

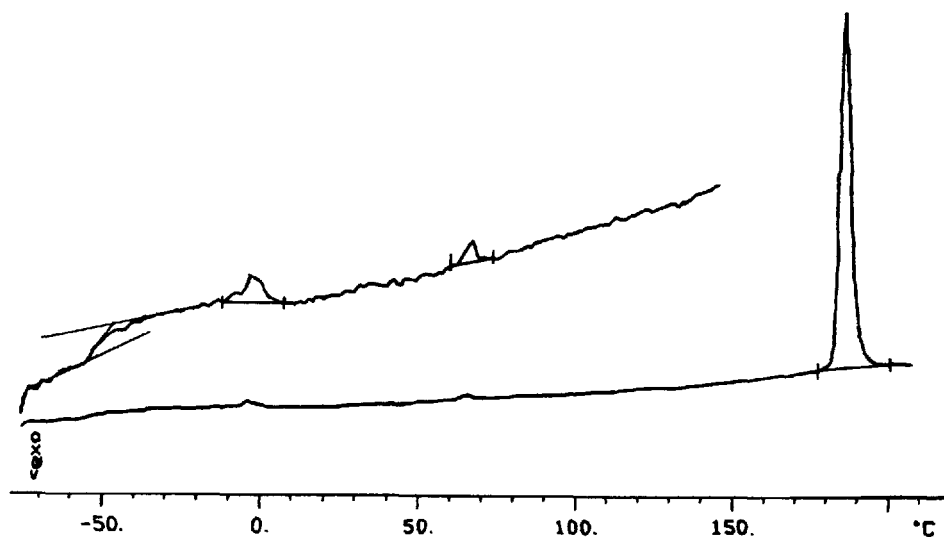


Figure 1. DSC-trace of the compound 2 (second heating run) including limits and baselines used for the calculation of transition enthalpies and change of heat capacity at the glass transition. The upper inset trace is enlarged 5 times.

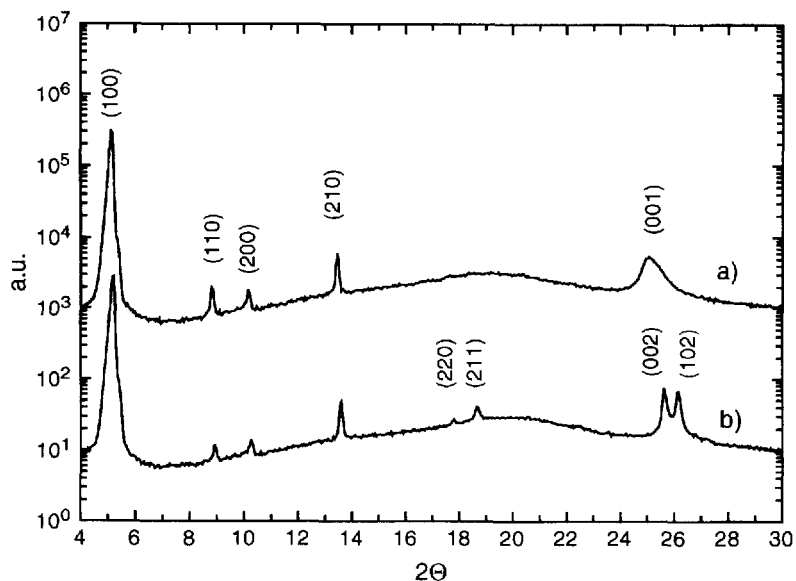


Figure 2. X-ray diffraction diagrams for compound 2: (a) $T = 88^\circ\text{C}$, D_{ho} phase; (b) $T = 21^\circ\text{C}$, D_{hp} phase.

Lattice constant a_{hex} , (hkl) indices and d -spacings (in Å) for the X-ray reflections in the D_{ho} phase (88°C) and in the D_{hp} phase (21°C) compared with values calculated from the a_{hex} values.

$T/^\circ\text{C}$	a_{hex}	(100)	(110)	(200)	(210)	(001)			
88	20.1	17.36	10.03	8.73	6.57	3.55			
calcd		17.41	10.05	8.70	6.58				
						(220)	(211)	(002)	(102)
21	19.9	17.09	9.90	8.65	6.52	4.98	4.74	3.47	3.41
calcd		17.23	9.95	8.62	6.51	4.98	4.75		

nature of the phase transition from the discotic plastic to the discotic hexagonal ordered phase we performed detailed X-ray measurements in relation to selected peaks at different temperatures. We determined the hexagonal lattice constant a_{hex} from the position of the (210) reflection peak and the distance of the molecules within the columns from the 'ordered' reflection in the discotic hexagonal ordered phase and from the (002) reflection in the discotic plastic phase, respectively. When comparing the 'ordered' reflection to the (002) reflection it must be kept in mind that the different peak profiles are in part due to the different dimensionality of the intracolumnar order. A saw-tooth shaped reflection with an infinitely steep slope towards low angles would be expected in the case of ideal one-dimensional intracolumnar order. This perfect shape is then smeared out by imperfections. For the determination of the intracolumnar distance in the D_{ho} phase it was therefore necessary to use the distance corresponding to the inflection point on the low angle side of the peak rather than the distance calculated from the maximum of the peak.

Figure 3 displays the intracolumnar and intercolumnar distances as a function of temperature. One interesting finding is that the phase transition is not accompanied by a change in the intercolumnar distance,

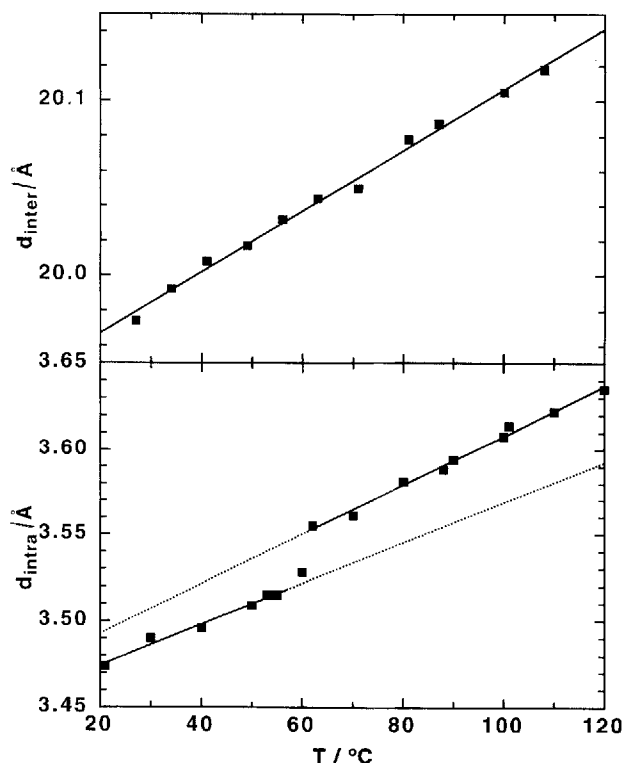


Figure 3. Inter- and intra-columnar lattice constants of compound **2**. The lines are linear regressions in the temperature range of the solid lines.

while the intracolumnar distance increases stepwise. The exact magnitude of the step in the intracolumnar distance must be looked at very carefully because of the different peak shapes and the different methods of determining the intracolumnar distance. However, we can state that there is only a small (less than 1 per cent) step. The smaller distance within the columns can be expected to give rise to an increased π -electron overlap which may be of importance for charge carrier mobilities. A general conclusion is that the density changes and thus the changes in the packing characteristic of this transition are small indeed.

Similar conclusions can be drawn from the analysis of the thermal expansion coefficients in the two phases. The thermal expansion coefficients are of the same order of magnitude as previously reported for the discotic hexagonal ordered phase of a similar compound [10]. We found a value of $0.9 \times 10^{-4} \text{K}^{-1}$ for the intercolumnar distance and for the intracolumnar distance, values of $3.4 \times 10^{-4} \text{K}^{-1}$ in the discotic plastic phase and $4.0 \times 10^{-4} \text{K}^{-1}$ in the discotic hexagonal ordered phase. The variation at the transition is small again.

Finally, we will attempt to draw some tentative conclusions on the perfection of the intracolumnar order in the different phases because of its importance for photoconductivity. The problem is that the shapes of the corresponding reflections differ for the reasons discussed above. We decided therefore to compare the low-angle sides of those reflections. For perfectly ordered mesophases, they should be infinitely steep in both cases, but it is apparent from figure 2 that the slope is much steeper in the discotic plastic phase. We use this observation to conclude that intracolumnar ordering is higher in the discotic plastic phase compared to that in the discotic hexagonal ordered phase.

The occurrence of the mixed reflections in the X-ray measurements seems to indicate that the lower temperature phase is in fact crystalline. Yet we observe in the DSC-curves a glass transition and we find that the material is not solid within this phase, but rather waxy. We thus decided to study the dynamic properties of the two phases discussed so far, using dielectric relaxation methods. The results are shown in figure 4 for both phases, i.e. the normal D_{ho} phase and the new phase. The analysis reveals that a relaxation occurs in this temperature region in both phases. To learn more about the nature of the relaxation we analysed the relaxation time distribution of this relaxation. It turned out to be symmetric in both phases and could therefore be represented by the Cole-Cole equation [11]

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau_0)^{(1-\alpha)}}$$

where α describes the broadening of the relaxation.

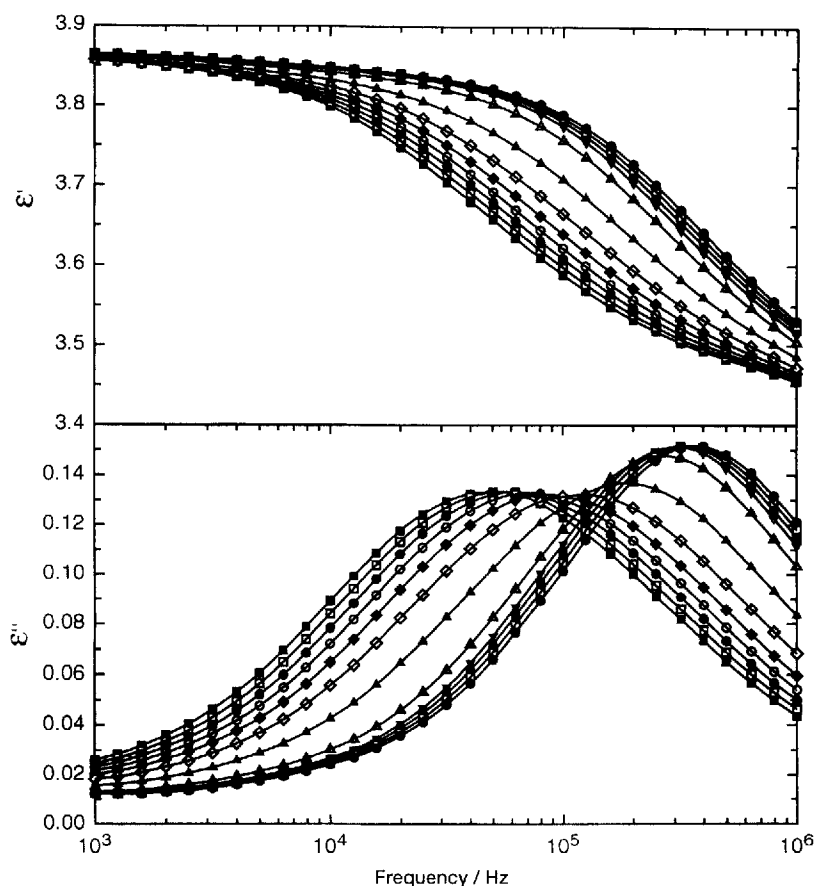


Figure 4. Real part ϵ' and imaginary part ϵ'' of the dielectric function versus frequency.

■ 63°C $\xrightarrow{1^\circ\text{C steps}}$ ● 74°C.

The relaxation time distribution is only weakly temperature dependent within the phase, and its width decreases slowly with increasing temperature. A significant change takes place at the phase transition as the parameter α jumps from 0.29 to 0.18. The relaxation time distribution is thus much broader in the lower temperature phase than in the D_{ho} phase, possibly because of the better correlation between the neighbouring molecules in the new phase.

The results on the relaxation strength and on the width of the relaxation time distribution are shown in figure 5. It is apparent that the relaxation strength $\Delta\epsilon$ decreases with increasing temperature and changes only slightly at the phase transition. The character of the rotational motion must therefore be similar in both phases. This relaxation has been attributed in the case of the D_{ho} phase to the freezing-in of the intracolumnar rotation [10] characteristic of the glass relaxation. These results indicate that rotational motions seem to take place not only in the D_{ho} phase but also in the new higher ordered phase.

There exists, however, one problem. Looking at the

activation diagram (see figure 6), this relaxation seems to be thermally activated within the new phase and the line does not approach the calorimetrically determined glass transition temperature exactly for 10^{-2} Hz as expected. The reason probably is that another phase transition takes place between this phase and the glass transition. The activation energy is high with the value of about 90 kJ mol^{-1} . The mean relaxation time increases by about half an order of magnitude at the phase transition and the activation energy decreases from 90 kJ mol^{-1} to about 60 kJ mol^{-1} in the D_{ho} phase. This is a typical value for the activation energy of discotic systems at temperatures 100 K above the glass transition, where the normally detected WLF-like behaviour [12] becomes an Arrhenius line. We thus still believe that the process is connected with the glass relaxation. We are currently not able to extend our frequency range sufficiently to solve this problem completely.

5. Conclusion

The tentative conclusion is that the disc-like molecules are able to perform intracolumnar rotations in the newly

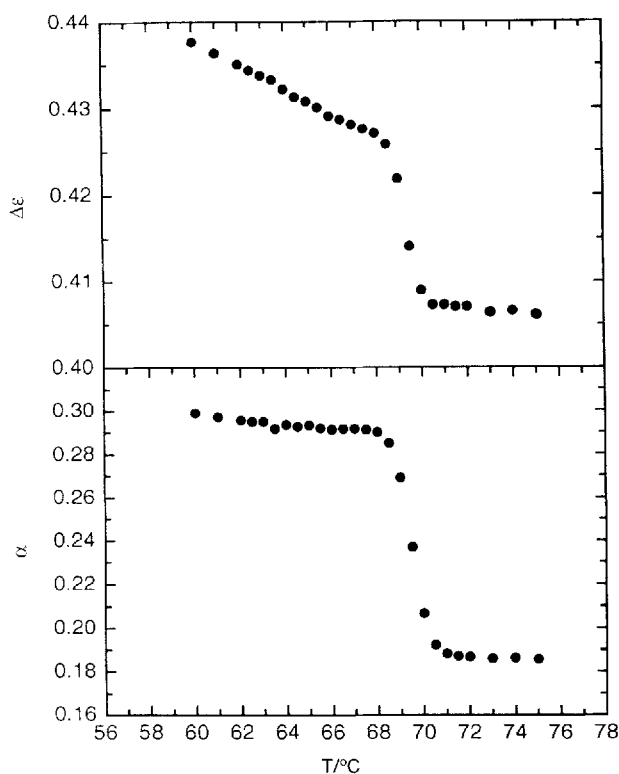


Figure 5. Dielectric relaxation strength $\Delta\epsilon$ and broadening parameter α versus temperature.

detected phase despite its three-dimensional registry. This is the reason why we propose to call this phase a plastic hexagonal columnar liquid crystalline phase D_{hp} . An interesting feature of this phase is that the intracolumnar repeat distance is twice that found for the normal columnar phase, apparently due to a corresponding

intracolumnar correlation of pairs of molecules. We believe that this novel phase is not unique for the compound studied here. More recent results that we have show that such a phase also occurs in 2,3,6,7,10,11-hexabutyloxytriphenylene (H4T) and in 3,6,7,10,11-pentapentyloxytriphenylene-2-yl triflate [13]—either as the only mesophase or within a sequence of discotic phases—and that this phase is characterized by a specific texture. First photoconductivity measurements on H4T show that the charge-carrier mobility in the D_{hp} phase is significantly higher than in the D_{ho} phase of similar compounds [14].

It will be interesting to characterize the structure of the phase below -5°C and to study the dynamics at lower frequencies in this phase; this will be done in the future.

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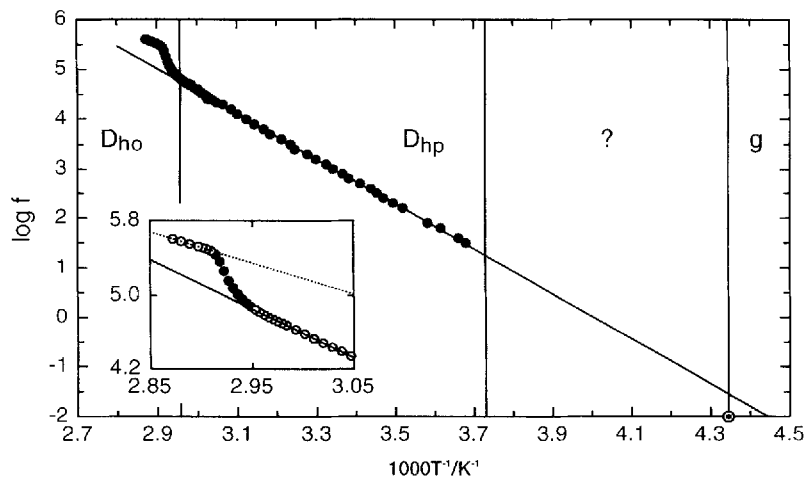


Figure 6. Arrhenius diagram for the glass-relaxation: ● mean relaxation times; ○ calorimetrically measured T_g ; — Arrhenius line in the D_{hp} -phase ($\Delta H = 90 \text{ kJ mol}^{-1}$). The inset shows the region of the transition in more detail: ○ data used for the Arrhenius-fits; ····· Arrhenius line in the D_{ho} phase ($\Delta H = 60 \text{ kJ mol}^{-1}$).

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