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Liquid Crystals

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Online publication date: 11 November 2010

To cite this Article Fimmen, W. , Glusen, B. , Kettner, A. , Wittenberg, M. and Wendorff, J. H.(1997) 'A re-entrant Col ho phase', Liquid Crystals, 23: 4, 569 — 573
To link to this Article: DOI: 10.1080/026782997208172
URL: http://dx.doi.org/10.1080/026782997208172

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LIQUID CRYSTALS, 1997, VOL. 23, NO. 4, 569–573

A re-entrant Col$_{ho}$ phase

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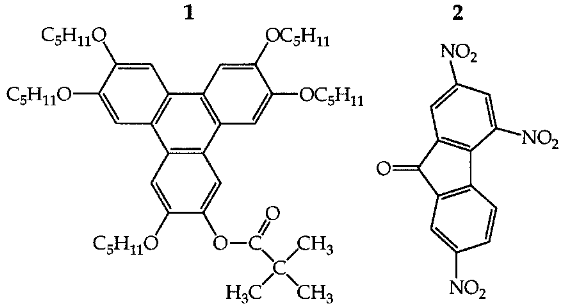
(*Received 24 March 1997; accepted 13 June 1997*)

The formation of a re-entrant columnar discotic hexagonal ordered phase (re-entrant Col$_{ho}$ phase) is reported for the asymmetrically substituted triphenylene 3,6,7,10,11-pentapentyloxytriphenylene-2-yl pivaloate (pivaloate) and its structural and dynamic properties described. The re-entrant phase behaviour is strongly modified by doping the pivaloate with the electron acceptor 2,4,7-trinitrofluorenone (TNF).

1. Introduction

A common observation for the sequence of liquid crystalline phases of a given compound is that the order increases with decreasing temperature at each phase transition [1, 2]. Typical sequences for calamitic systems are, for instance, isotropic–nematic–smectic A and possibly crystalline. Yet quite a large number of calamitic compounds are known today which display re-entrant phases: an ordered phase is then located on the temperature scale between two less ordered phases [1–3].

The existence of re-entrant phases also in liquid crystal materials composed of disc-like molecules was first suggested in 1979 [4] in analogy to calamitic mesogens. Tinh and co-workers obtained an inverted phase sequence for hexa-alkanoyloxytruxenes with short alkyl chains; a transition into a highly fluid nematic phase was observed on cooling from a more viscous rectangular columnar phase [5, 6]. The same authors reported in 1981 the existence of re-entrancy in a pure truxene derivative at atmospheric pressure [7], the more ordered columnar phase being stable above and below the temperature range in which a nematic discotic phase is stable. Re-entrant nematic discotic phases were also observed for hexa(*p*-alkoxybenzoyloxy)truxenes with long alkoxy chains [8]. To our knowledge re-entrant columnar phases composed of disc-like molecules have so far been detected only for truxene derivatives. We report in this contribution a re-entrant behaviour of a triphenylene compound, a pivaloate derivative (see scheme 1), and discuss the effect on the re-entrant behaviour of doping the compound with the electron acceptor TNF.



Scheme 1. Chemical formulae of the discotic pivaloate **1** and the electron acceptor TNF **2**.

2. Characterization techniques

Transition temperatures were determined by differential scanning calorimetry (Mettler DSC30) with a heating rate of $10\,\mathrm{K\,min^{-1}}$. The structure was analysed using wide angle X-ray scattering (WAXS). Scattering curves were obtained using a Siemens D-5000 diffractometer; Ni-filtered CuKα radiation was used in all cases. The temperature was controlled within 1 K.

The relaxation behaviour was analysed using dielectric relaxation spectroscopy, covering a frequency range from 10^{-2} Hz to 1 MHz (Schlumberger Solartron and HP 4284A). A nitrogen gas heating system 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 on gold covered electrodes made of stainless steel by coating in the isotropic state.

The charge transfer (CT) complexes were obtained by dissolving the compounds in tetrahydrofuran, stirring the mixture for 1 h at room temperature and evaporating the solvent.

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3. Results and discussion

3.1. *Undoped systems*

3,6,7,10,11-Pentapentyloxytriphenylene-2-yl pivaloate exhibits three endothermic transitions on heating and a glass transition as reported previously [10]. The compound displays a Col$_{\text{ho}}$ phase between 65 and 178°C below the temperature range of the isotropic melt and a new plastic columnar discotic phase Col$_{\text{hp}}$ below 65°C characterized by a three-dimensional crystal-like registry [10]. We report in the following text the results of X-ray measurements performed below room temperature to identify the structure of a low temperature phase between -5°C and the glassy state.

Figure 1 displays the X-ray diagrams of the high temperature hexagonal phase, 1 (*a*), of the plastic phase, 1 (*b*) and finally of the low temperature phase, 1 (*c*). The X-ray diagram of the low temperature phase is characterized by several Bragg peaks which can be assigned to a two-dimensional hexagonal lattice with a lattice constant of $a_{\text{hex}} = 20$ Å (see table 1). The halo in the wide angle regime is caused by the packing of the disordered alkyl chains and the broad asymmetric peak at 3·44 Å defines the intracolumnar order. No mixed reflection ($h\,k\,l$) indicating correlations between the two-dimensional hexagonal lattice ($h\,k\,0$) and the one-dimensional ordering within the columns (0 0 1) occurs. The crystal-like three-dimensional registry characteristic of the plastic phase Col$_{\text{hp}}$ is thus destroyed not only by heating to higher temperatures, but also by cooling to lower temperatures, i.e. a re-entrant Col$_{\text{ho}}$ phase is observed. The phase sequence is thus:

$$[\mathrm{g}\ -43\ (\Delta C_{\mathrm{p}} = 15\,\mathrm{J\,g^{-1}\,K^{-1}})\ \text{re-entrant Col}_{\text{ho}}\ -5\ (0{\cdot}5)\ \text{Col}_{\text{hp}}\ 65\ (0{\cdot}4)\ \text{Col}_{\text{ho}}\ 178\ (20{\cdot}3)\ \mathrm{I}]$$

transition temperatures are given in °C and transition energies (in brackets) in kJ mol^{-1}.

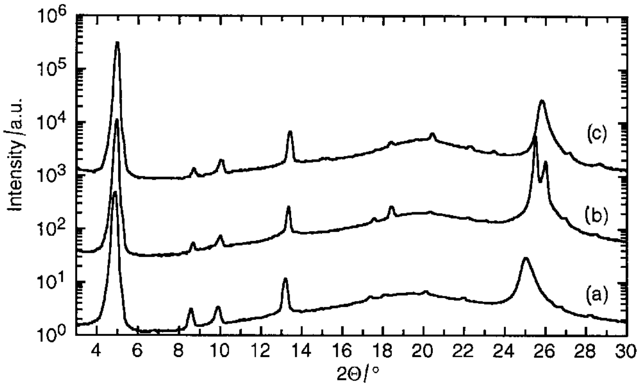


Figure 1. X-ray diffraction diagrams for the different phases: (*a*) Col$_{\text{ho}}$ phase (88°C), (*b*) Col$_{\text{hp}}$ phase (21°C), (*c*) re-entrant Col$_{\text{ho}}$ phase (-15°C).

Table 1. *d*-Spacings for the X-ray reflections in the re-entrant Col$_{\text{ho}}$ phase (-15°C) compared with values calculated from the value of a_{hex} (20·07 Å).

	d-Spacing Å	
Indices ($h\,k\,l$)	Observed	Calculated
(100)	17·7	17·4
(110)	10·0	10·0
(200)	8·8	8·7
(210)	6·57	6·57
(310)	4·81	4·82
(400)	4·34	4·34
(320)	3·98	3·99
(410)	3·79	3·79
(420)	3·27	3·28
(510)	3·11	3·12
(001)	3·46	—

The X-ray diagrams characteristic of the high and low temperature Col$_{\text{ho}}$ phase are thus very similar on a qualitative basis. In order to elucidate the differences in the nature of the two phases we investigated their structural and dynamic properties in more detail.

We determined, for this purpose, the lattice constant a_{hex} from the position of the (2 1 0) reflection peak and the spacing of the molecules within the columns from the 'ordered' reflection in the columnar hexagonal ordered phase and from the (0 0 2) reflection in the columnar plastic phase, respectively. When comparing the 'ordered' reflection with the (0 0 2) reflection one has to keep in mind that the different peak profiles are in part due to the different dimensionality of the intracolumnar order. In the case of an ideal one-dimensional order, a saw-tooth shaped reflection with an infinitely steep slope towards low angles would be expected [11]. This perfect shape is then smeared out by imperfect ordering and a finite disk radius. It is therefore necessary to analyse carefully the shape of the peak in order to obtain the exact value of the intracolumnar distance [11].

The variations of the intracolumnar and intercolumnar distances obtained in this way are shown in figures 2 (*a*) and 2 (*b*) as a function of temperature. The hexagonal lattice constant increases linearly with increasing temperature in the re-entrant phase as well as in the plastic phase. The lattice constant becomes approximately independent of the temperature at elevated temperatures in the Col$_{\text{ho}}$ phase. The transition between the various phases seems to be almost continuous as far as the lattice dimensions are concerned. A closer inspection reveals tiny stepwise variations at the transitions and shows that the lattice constant remains constant within 10 K around the temperature of the transition to the high temperature Col$_{\text{ho}}$ phase. The intracolumnar distance displays a small stepwise change at the transition

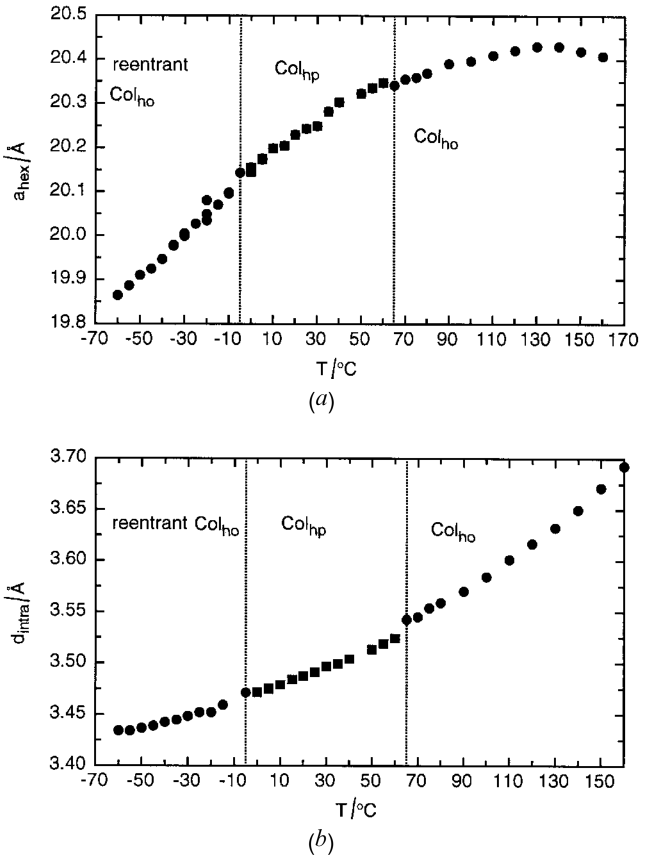


Figure 2. (a) Hexagonal lattice constant versus temperature for the different phases: ● Col$_{ho}$ phase, ■ Col$_{hp}$ phase. The absolute values of a_{hex} have an error of about one percent, but this is much less for their relative position over the temperature range. The previously published values are within the error interval. (*b*) Intracolumnar distance of the molecules versus temperature for the different phases: ● Col$_{ho}$ phase, ■ Col$_{hp}$ phase.

from the plastic phase to the high temperature Col$_{ho}$ phase.

The values obtained for the thermal expansion coefficients are of the same order of magnitude as those previously reported for the columnar hexagonal ordered phase of a similar compound [12] and in good agreement with results from dilatometric studies of the plastic phase and the high temperature Col$_{ho}$ phase [13]. The values are displayed in table 2. It is obvious that the two Col$_{ho}$ phases differ strongly with respect to the anisotropy of the thermal expansion. The coefficient is six times larger for the intracolumnar direction compared with the intercolumnar directions in the high temperature phase, whereas the expansion is nearly isotropic in the low temperature phase. The plastic phase shows an intermediate behaviour; the calculated volume expansion coefficient is higher in the low temperature Col$_{ho}$ phase compared with the other two phases.

Table 2. Thermal expansion coefficients α for the expansion in the direction of the column axis ($\alpha_\parallel$) and perpendicular to the column axis ($\alpha_\perp$).

Phase	$\alpha_\perp$ [K^{-1}]	$\alpha_\parallel$ [K^{-1}]
Col$_{ho}$	$0{\cdot}7\times10^{-4}$	$4{\cdot}2\times10^{-4}$
Col$_{hp}$	$1{\cdot}6\times10^{-4}$	$3{\cdot}0\times10^{-4}$
Re-entrant Col$_{ho}$	$2{\cdot}4\times10^{-4}$	$2{\cdot}4\times10^{-4}$

In the following we will describe the results of studies on the dynamics of the different phases displayed by the pivaloate using dielectric relaxation spectroscopy. We observe one relaxation in all three phases. It has been attributed to the glass relaxation connected with the freezing-in of the intracolumnar rotation [14]. The character of the relaxation is, however, different in the different phases, as is apparent from a more detailed analysis of the data.

The time distribution of the relaxation was found to be symmetric in all phases. We analysed it on the basis of the Cole–Cole equation [15]

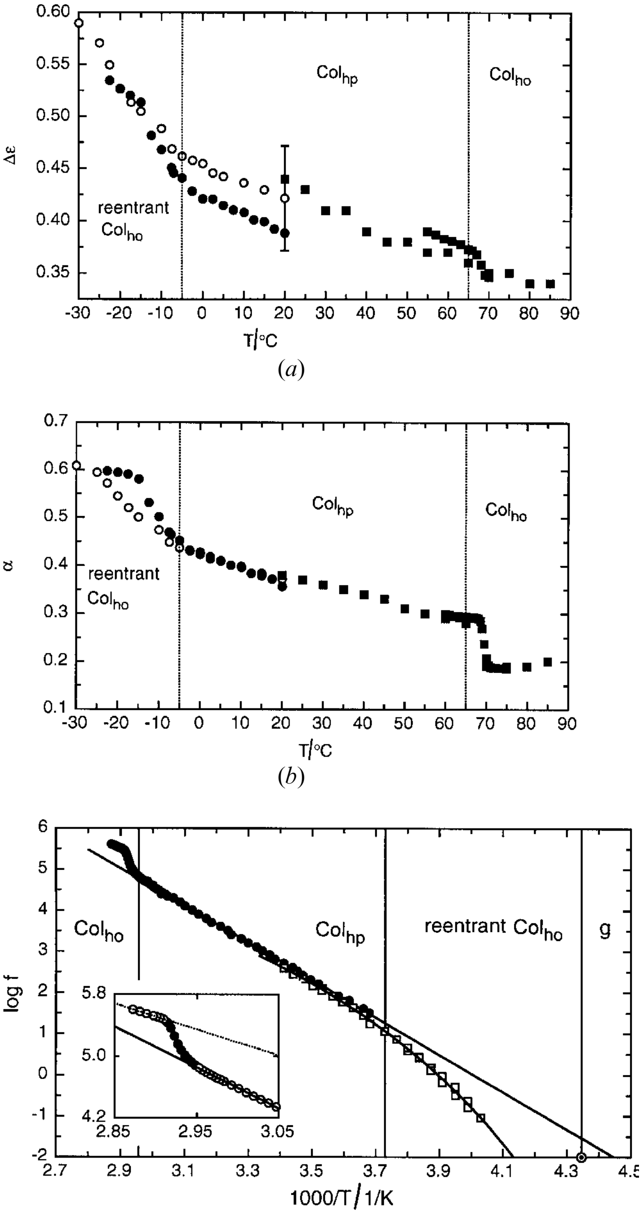
$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau_0)^{(1-\alpha)}},$$

where α describes the broadening of the relaxation. An additional contribution observed in the low frequency range can be attributed to the onset of electrical conductivity within the sample. Its frequency dependence follows the law $\varepsilon'' \propto \omega^{-s}$, with $s = 0{\cdot}5$–1.

The results for the relaxation strength and the width of the relaxation time distribution are shown in figures 3(*a*) and 3(*b*) for the temperature range covering all phases discussed here [10].

The relaxation strength increases with decreasing temperature from 0·35 to 0·6. The relaxation strength changes in a stepwise manner, but only weakly so at the transition from the Col$_{ho}$ to the plastic phase and more strongly, yet more continuously, at the transition to the re-entrant phase.

The relaxation time distribution is only weakly temperature dependent within the phases, its width decreasing slowly with increasing temperature. Significant changes take place at the phase transitions as the parameter α jumps from 0·6 (re-entrant Col$_{ho}$) to 0·42 in the plastic phase, decreases to 0·3 within the plastic phase and then jumps to 0·18 (Col$_{ho}$). The first step is much broader and covers a temperature range of 10 K, whereas the second step occurs within 2 K. It is thus apparent that the relaxation behaviour of all three phases has the same origin—rotations of the columns [14]—but that the phases differ with respect to the details of this relaxation process. The two hexagonal phases differ strongly both in the relaxation strength and in the width of the relaxation time distribution.



(*a*)

(*b*)

(*c*)

Figure 3. (*a*) Relaxation strength Δε versus temperature: ■,● heating curves, □ cooling curve. Due to a variation in the thickness of the sample of about 10%, the absolute value of the relaxation strength is relatively inexact (error bar plotted for only one value). Also the thermal history has an influence on the absolute value because of orientation effects. Nevertheless, the relative error within one series over the temperature range is much smaller so that one can get all the information about the temperature behaviour of the relaxation strength. One interesting observation is that the changes in the relaxation behaviour occur within the temperature regions of the Col$_{ho}$ phases, 5–10 K above and below the transition temperatures obtained from DSC and X-ray studies. (*b*) Broadening parameter α versus temperature: ■,● heating curves, □ cooling curve. (*c*) Activation diagram for the glass relaxation: ● measured on HP4284A, □ measured on Schlumberger Solartron.

The activation diagram displayed in figure 3 (*c*) reveals an interesting feature: the relaxation is thermally activated in the plastic phase with an activation energy of 90 kJ mol^{-1} [10]. Such a behaviour is usually not found for the glass relaxation process in organic glasses which are fragile glasses; it is characteristic of strong glasses [16]. We thus tentatively interpret the activation diagram obtained for the plastic columnar phase as an indication of the formation of a strong rather than a fragile glass. We obtained similar results for other compounds displaying the plastic phase [17]. Yet this behaviour changes to a WLF behaviour [18], as usually found for the glass transition in organic materials, at the transition into the re-entrant hexagonal phase. The WLF parameters $C_1=10$ and $C_2=55$ K are typical for glass relaxations in organic materials. The extrapolation of the WLF curve to a characteristic frequency of 10^{-2} Hz leads to a glass transition temperature of −31°C which is located 10 K above the calorimetrically determined glass transition temperature of −43°C. We have to point out that we often observe such a discrepancy for ordered glasses; there are also examples where T_g(DSC) > T_g(DK 10^{-2} Hz) [19].

3.2. *Doped systems*

The usual finding for discotic triphenylenes doped with an electron acceptor is that a columnar phase is stabilized or even induced in non-columnar systems due to the formation of charge transfer complexes [20]. We therefore decided to study the effect of doping on the stability of the more ordered plastic columnar phase and on the re-entrant behaviour. We therefore doped the pivaloate derivative with an amount of TNF ranging between 0·5 and 4 mol %.

Differential scanning calorimetry reveals only the transition to the isotropic liquid at 179°C in the second heating run for the mixture with 2 mol % TNF. Neither a glass transition nor the transitions re-entrant Col$_{ho}$–Col$_{hp}$–Col$_{ho}$ could be detected by DSC investigations, apparently due to the small enthalpy changes. Temperature dependent X-ray measurements revealed, however, that the phase behaviour in the CT complexes doped with small amounts of TNF (0·5–3 mol %) is the same as in the undoped compound. The temperature range in which the Col$_{hp}$ phase is observed is, however, strongly modified by the doping (figure 4). The observation is that the plastic hexagonal phase is shifted to lower temperatures compared with the pure compound and that the width of the Col$_{hp}$ phase decreases with increasing content of TNF from 85 K (0·5 mol % TNF) to 15 K (3 mol % TNF). The higher ordered plastic columnar phase is suppressed and consequently also the re-entrant phase behaviour for the CT complexes for concentrations of 4 mol % TNF or more.

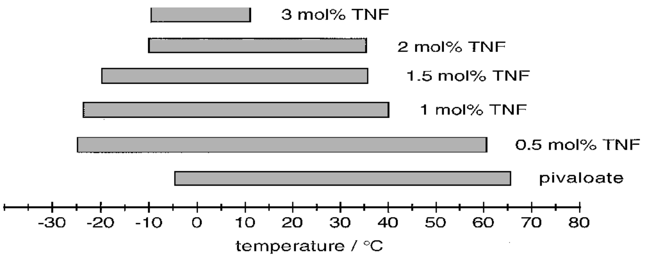


Figure 4. Temperature range of the Col$_{hp}$ phase for pure pivaloate and mixtures with TNF.

4. Conclusion

A re-entrant behaviour was observed for a pure triphenylene derivative and for CT complexes with small concentrations of an electron acceptor. A columnar hexagonal plastic phase neighbours two hexagonal ordered phases, one on the high and one on the low temperature side. The origin of this re-entrant phenomenon is still unknown, but we believe that it may be of a similar nature to that found for re-entrant phases of calamitic mesogens where the driving force is related to the dimerization of strongly polar molecules [21]. In fact, the formation of dimers in columns has been observed in the crystalline phases of symmetric triphenylene derivatives using X-ray diffraction [22] and electron microscopy [23].

The X-ray data indicate the presence of dimers in the Col$_{hp}$ phase discussed here. We speculate that there might be a temperature range in which dimerization is thermodynamically favoured. Our assumption is that the dimers are staggered rather than stacked vertically on top of each other (figure 5). ^{13}C NMR data show different electron densities in different regions of the triphenylene core [10, 19]; a staggered conformation would thus be electronically more stable. Columns of these staggered dimers would favour a three-dimensional registry because of interdigitation; staggered columns would need more space on a hexagonal lattice than unstaggered columns. Upon cooling, we observe a contraction of the hexagonal lattice. We assume that steric factors begin to outweigh the electronic factors at a particular temperature and that the staggered dimers are destroyed. The driving force for a three-dimensional order is lost and a re-entrant Col$_{ho}$ phase occurs. A rotation of molecules is possible at all times, although we are unable to specify whether the molecules rotate individually or as pairs.

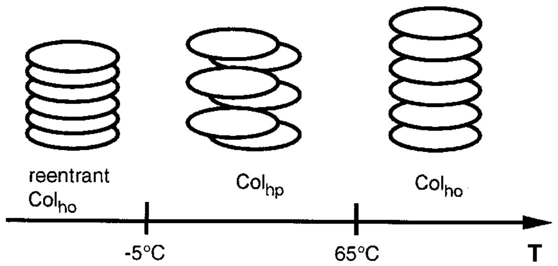


Figure 5. Molecular arrangement within the columns which we propose for the different columnar phases. In all three phases, the columns are arranged on a hexagonal lattice, but only in the plastic phase are the columns correlated and unable to be shifted against each other.

We gratefully acknowledge the financial support by the Deutsche Forschungsgemeinschaft (SFB 383: Unordnung in Festkörpern auf mesoskopischen Skalen).

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