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Preliminary communication

Enantiotropic and monotropic transitions of the discotic mesogen 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrin under pressure

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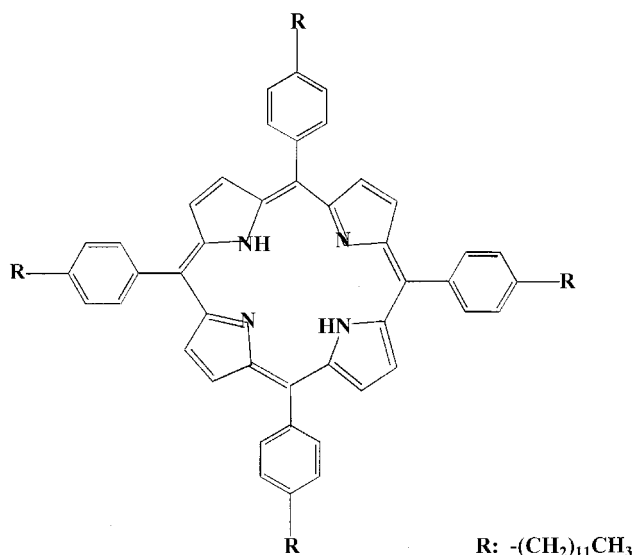
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The crystal and mesophase transitions of the discotic material 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrin have been studied by high pressure DTA and wide angle X-ray diffraction. At lower pressures, the discotic lamellar (D_L) phase is enantiotropic, but at higher pressures above a critical point determined as 240 MPa and 170°C the D_L phase is monotropic.

Since disk-like mesogens were found by Chandrasekhar *et al.* [1] in 1977 and other groups [2, 3] in 1979, the mesomorphic states of such materials have been studied for their intriguing chemical and physico-chemical properties and mesomorphic structures. Goodby *et al.* [4] reported in 1980 that uro-porphyrin I octa-*n*-dodecylester shows a monotropic mesophase within a very narrow temperature range of 0.1°C. Then Ohta *et al.* [5] found the discotic lamellar phase of the transition metal complexes known as bis[1,3-di(*p*-*n*-alkoxyphenyl)propane-1,3-dionato]copper(II) (abbreviated to C_nO-Cu , $n = 6-12$). They deduced that the mesophase is truly a new discotic lamellar phase (D_L) and that it has a structure in which the molecules tilt to the layers. Shimizu *et al.* [6, 7] also found that metal-free 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrin, hereafter abbreviated to C12TPP, exhibits a peculiar D_L phase and shows an interesting mesomorphic transition. However, knowledge of the mesomorphic properties of different discotic mesogens [8, 9] up to present is relatively sparse.

The chemical structure of C12TPP is shown below.



C12TPP shows the reversible phase transformations low- to high-temperature crystal (Cr_2-Cr_1), Cr_1-D_L , and D_L -isotropic liquid (I). We have now investigated the thermal and structural behaviour of C12TPP under

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hydrostatic pressures up to 300 MPa by high pressure differential thermal analysis (DTA) and wide angle X-ray diffraction (WAXD) methods. We present here preliminary experimental results on the phase transitions and new evidence for the monotropic nature of the D_L phase under high pressures above a critical pressure, while the D_L phase appears reversibly between the Cr_1 crystal and isotropic phases under lower pressures [10].

C12TPP was prepared by the usual synthetic approach from tetraphenylporphyrin [9] and was purified by column chromatography after oxidation of chlorinated by-product. Further purifications were carried out by Soxhlet extraction of impurities with methanol-acetone. Finally, the product was recrystallized from a benzene-acetone (10/90 v/v) mixture.

The structural behaviour of C12TPP was studied by using a rotating anode X-ray generator (60 kV and 200 mA; Rotaflex RU-200, Rigaku Co.) equipped with a high pressure vessel on the goniometer. The high pressure wide angle X-ray diffraction (WAXD) system was designed to be operated at pressures up to 500 MPa in a temperature region between -30°C and 300°C . Pressure is measured within an accuracy of ± 1 MPa by a manganin gauge calibrated against a precision Broudon gauge (Heise, type CM, Dresser-Industries, Inc.). Temperature is measured with a sheathed C-A thermocouple attached to a beryllium spindle which is used as a sample vessel and also X-ray window. The sample in the beryllium spindle is pressurized hydrostatically with low viscosity dimethylsilicone oil (10 centiStokes) and is irradiated by a beam of Ni-filtered Cu K_α X-rays. The diffracted X-rays are detected by a position-sensitive proportional counter (PSPC-30, Rigaku Co.) covering diffraction angles of $2\theta = 28^\circ$ on the equator. Thermal behaviour was studied by a high-pressure DTA apparatus described elsewhere [11]. The high pressure DTA system was operated in the temperature region between -20°C and 250°C under hydrostatic pressures up to 300 MPa. Medium viscosity dimethylsilicone oil (100 centiStokes, Toshiba Silicone Co.) was used as a pressure transmitting medium. The DTA runs were performed at a constant scanning rate of 5°C min^{-1} under various pressures.

Figure 1 shows the temperature dependence of the X-ray patterns of the Cr_2 crystal of C12TPP which was obtained by cooling from the isotropic state at atmospheric pressure. The X-ray pattern of Cr_2 is maintained until the Cr_2 - Cr_1 transition occurs at about 38.5°C . Then the X-ray pattern of the Cr_1 crystal is maintained until temperatures up to about 60°C . Further heating of the sample induces a very strong reflection of the D_L phase at low angles over a wide temperature region between 60°C and 150°C , until the strong reflection disappears completely at the D_L -I transition at about 155°C . The D_L phase exhibits a very strong

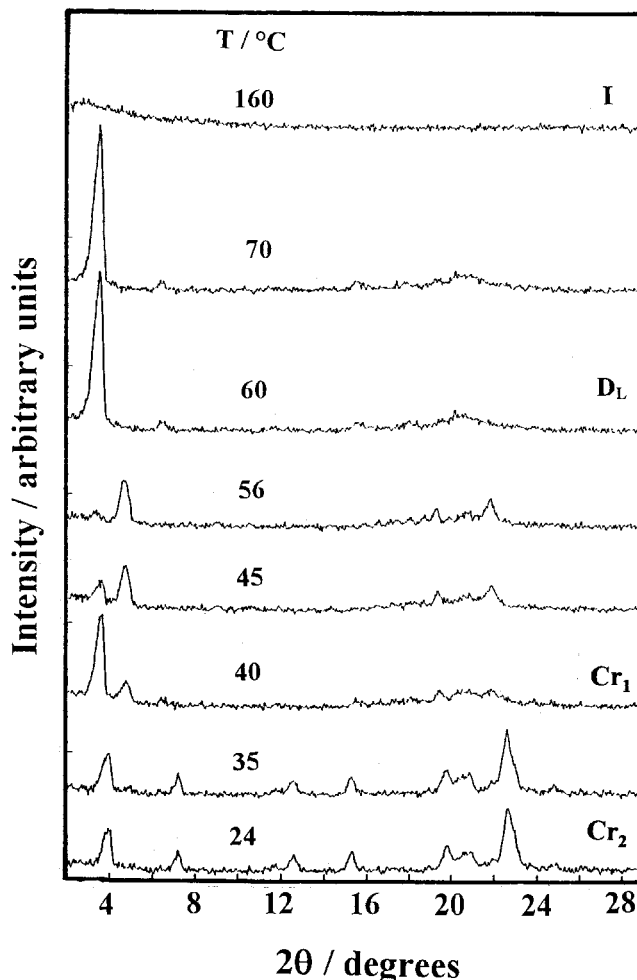


Figure 1. X-ray patterns of crystal Cr_2 of the porphyrin C12TPP on heating at atmospheric pressure: Cr_2 crystal at $24 \sim 38^\circ\text{C}$, Cr_1 crystal at $40 \sim 60^\circ\text{C}$, D_L phase at $60 \sim 150^\circ\text{C}$, and isotropic liquid at 155°C .

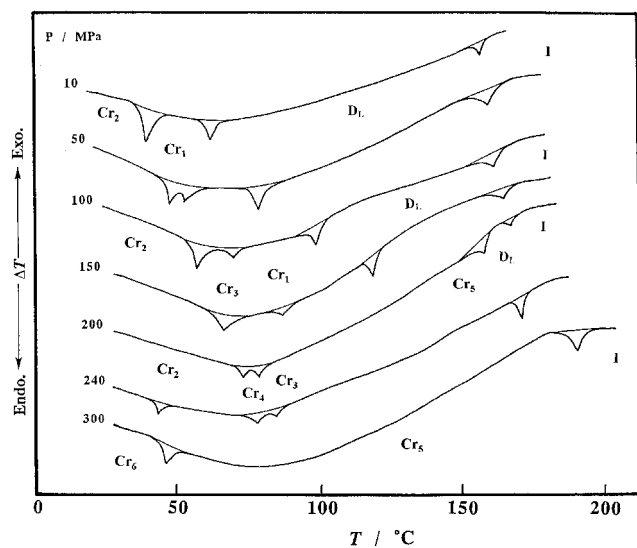


Figure 2. High pressure DTA curves of C12TPP.

reflection at $2\theta = 3.42^\circ$ ($d = 25.78 \text{ \AA}$) and several weak reflections at wide angles. The X-ray pattern in this study is the same as that of the discotic lamellar D_L phase reported previously by Shimizu *et al.* [6]. According to the CPK molecular model shown by Ohta *et al.* [5], the d spacing of the low-angle reflection represents the distance between neighbouring C_nO groups in the discotic liquid crystal of the transition metal complex. So it can be taken that the d spacing of the low angle reflection of C12TPP is the distance between the neighbouring alkylphenyl groups. The structural changes in the X-ray pattern correspond well to the DSC thermal behaviour, and they are reversible for the Cr_2 - Cr_1 - D_L -I process at atmospheric pressure.

Figure 2 shows the DTA heating curves of C12TPP under various pressures. As observed from the DSC thermal behaviour at atmospheric pressure, the enantio-

tropic transitions Cr_2 - Cr_1 - D_L -I are observed at 10 MPa. Application of hydrostatic pressure to the sample induces successively two crystal polymorphs (Cr_3 , Cr_4) between the Cr_2 and Cr_1 crystal phases at intermediate temperatures. As shown in figure 2, the transition processes Cr_2 - Cr_3 - Cr_1 - D_L -I and Cr_2 - Cr_4 - Cr_3 -(Cr_1)- Cr_5 - D_L -I are observed in the pressure regions 20–180 and 180–200 MPa, respectively. On the other hand, the temperature region of the D_L phase decreases remarkably from 110°C at 0.1 MPa to about 10°C at 200 MPa because the Cr_1 - D_L transition temperature increases linearly with increasing pressure, while the D_L -I transition temperature is only slightly dependent upon pressure. Therefore the stable region of the D_L phase forms a triangle in the T vs P diagram which is measured on heating. The critical point of the D_L phase on heating is determined to be around 240 MPa and 170°C [10]. The

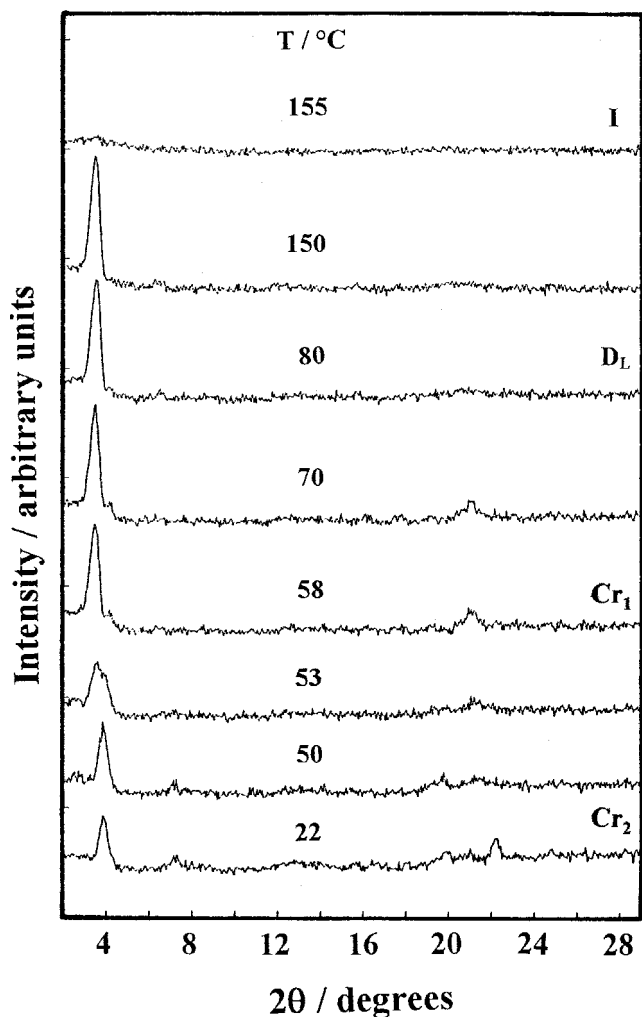


Figure 3. X-ray patterns of crystal Cr_2 of the porphyrin C12TPP on heating at 50 MPa: Cr_2 crystal at $22 \sim 50^\circ\text{C}$, Cr_1 crystal at $54 \sim 70^\circ\text{C}$, D_L phase at $80 \sim 150^\circ\text{C}$, and isotropic liquid at 155°C .

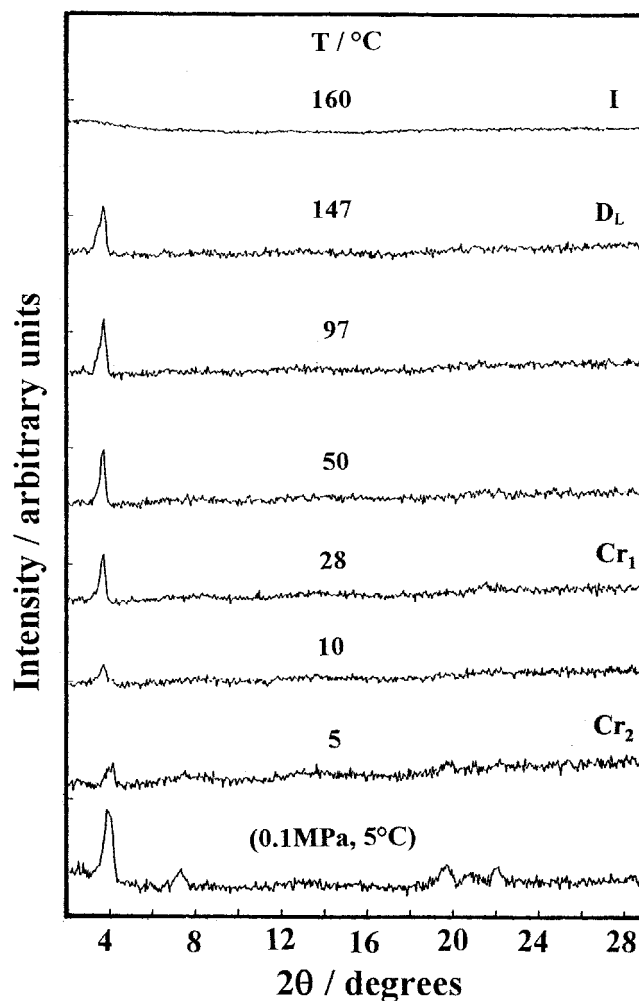


Figure 4. X-ray patterns of C12TPP on the subsequent cooling at 50 MPa: isotropic liquid at 160°C , D_L phase at $150 \sim 90^\circ\text{C}$, Cr_1 crystal at $50 \sim 28^\circ\text{C}$, and Cr_2 crystal at $10 \sim 5^\circ\text{C}$.

existence of a critical point for a discotic liquid crystal material has already been found for benzene-hexa-*n*-octanoate, BH8, by Chandrasekhar *et al.* [1]. BH8 has a liquid crystal phase structure in which there is lamellar order with hexagonal symmetry in two dimensions and liquid-like disorder in the third. The critical point of the compound was estimated to be 1.4 kbar and 97°C. Therefore, the finding of the critical point of the D_L phase of C12TPP is the second recorded example. No thermal transition related to the D_L phase seems to be found at high pressures above 240 MPa. Application of high pressures (for example, 300 MPa) to the sample induces simply two transitions at low and high temperatures, and the associated peaks are related to the sixth to fifth (Cr_6 – Cr_5) crystal transition and the Cr_5 –I transition at low and high temperatures, respectively. The thermal behaviour at these high pressures is expressed by the transformation of $Cr_6 \leftrightarrow Cr_5 \leftrightarrow I$. In the

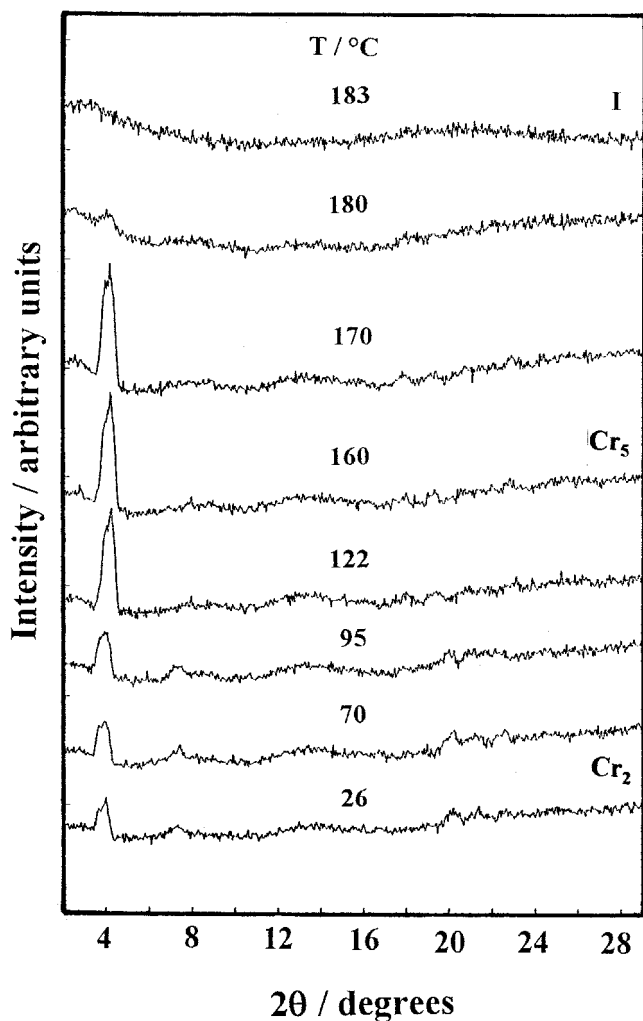


Figure 5. X-ray patterns of crystal Cr_2 of the porphyrin C12TPP on heating at 300 MPa: Cr_2 crystal at 26 ~ 95°C, Cr_5 crystal at 122 ~ 180°C, and isotropic liquid at 183°C.

pressure region between 200 and 250 MPa, however, a complex thermal behaviour is observed: the Cr_2 and Cr_6 crystals are formed concurrently via the two different processes $I \rightarrow D_L \rightarrow Cr_1 \rightarrow Cr_3 \rightarrow Cr_2$ and $I \rightarrow Cr_5 \rightarrow Cr_6$.

In order to check the structural behaviour of C12TPP under pressure, we performed wide angle X-ray diffraction (WAXD) experiments at 50 and 300 MPa. Figures 3 and 4 show the X-ray patterns of Cr_2 on heating and subsequent cooling at 50 MPa, respectively. The transformation process of Cr_2 –(Cr_3)– Cr_1 – D_L –I is observed on heating at 50 MPa and subsequent cooling gives clearly the reverse process. Unfortunately the Cr_3 phase could not be recognized clearly, possibly because of weak reflections and the small temperature region of the Cr_3 phase. It is noted that the strong low angle reflection characteristic of the D_L phase is observed reversibly at

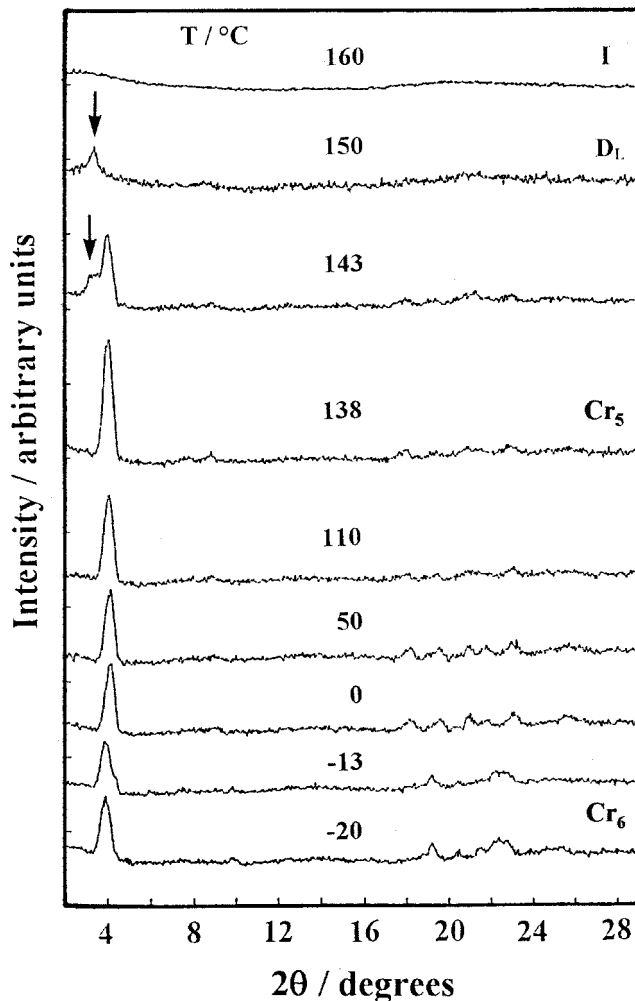


Figure 6. X-ray patterns of C12TPP on the subsequent cooling from the isotropic liquid at 300 MPa: isotropic liquid at 185 ~ 160°C, D_L phase at 150 ~ 145°C, $D_L \rightarrow Cr_5$ transition at 143°C, Cr_5 crystal at 138 ~ –10°C, and Cr_6 crystal at –13 ~ –20°C.

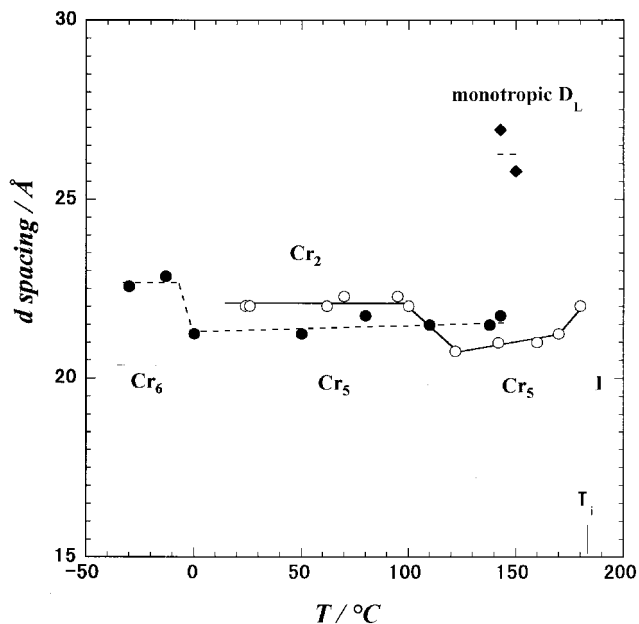


Figure 7. Temperature dependence of the d spacing of the low angle reflection at 300 MPa. Open and full symbols are for measurements made on heating and subsequent cooling processes, respectively.

$2\theta = 3.52^\circ$ ($d = 25.07 \text{ \AA}$). Figure 5 shows the X-ray patterns of the same Cr_2 crystal on heating at 300 MPa, Cr_2 being the low-temperature form at atmospheric pressure. Cr_2 is maintained at temperatures up to 95°C and then the Cr_2 –(Cr_4 , Cr_3)– Cr_5 transition sequence occurs, beginning at about 100°C . The X-ray pattern of the Cr_5 crystal continues over a wide temperature region between 100

and 180°C , until the crystal reflections disappear completely at 183°C . The X-ray pattern of Cr_5 is clearly different from that of the D_L phase; Cr_5 exhibits a strong reflection at $2\theta = 4.16^\circ$ ($d = 21.24 \text{ \AA}$) and several reflections at different wide angles. The heating experiment at 300 MPa therefore indicates the Cr_2 – 100°C – Cr_5 – 183°C – I transformation. In this case too, the small Cr_4 – Cr_3 transition observed on the DTA curve was not confirmed clearly by the structural behaviour at 300 MPa. Figure 6 shows the X-ray patterns of C12TPP on subsequent cooling from 185°C at 300 MPa. A small but sharp reflection at $2\theta = 3.42^\circ$ ($d = 25.78 \text{ \AA}$) is observed in a small temperature region between 150 and 143°C . This reflection is characteristic of the D_L phase which is observed reversibly at 0.1 and 50 MPa. This is clear evidence of the monotropic nature of the D_L phase which appears only on cooling at 300 MPa. The cooling experiment at 300 MPa shows the $\text{I} \rightarrow \text{D}_L$ transition at about 150°C followed by the $\text{D}_L \rightarrow \text{Cr}_5$ transition at about 143°C . Cr_5 displays a strong reflection at $2\theta = 4.11^\circ$ ($d = 21.49 \text{ \AA}$) and several wide angle reflections. Further cooling exhibits the $\text{Cr}_5 \rightarrow \text{Cr}_6$ crystal transition at very low temperatures (-13°C). The change in d spacing of the low angle reflection on heating and subsequent cooling at 300 MPa is shown clearly in figure 7. Reheating at 300 MPa showed the Cr_6 – Cr_5 – I transitions.

The table lists the Bragg spacings (d spacings) calculated from the reflection peaks of the various crystal phases and the D_L phase of C12TPP. The structural nature of the monotropic D_L phase seems to be the same as that of the D_L phase formed at atmospheric

Table. Bragg spacings (\AA) of the various crystalline phases and the D_L phase of C12TPP. Cr_1 and Cr_2 crystal phases were formed on cooling the sample from the isotropic state at atmospheric pressure; Cr_5 , Cr_6 crystal phases and the D_L phase were formed on cooling the sample at 300 MPa. vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

Atmospheric pressure			300 MPa		
Cr_2 (24°C)	Cr_1 (48°C)	D_L (100°C)	Cr_6 (-20°C)	Cr_5 (138°C)	monotropic D_L (150°C)
24.07 m	24.73 w 18.61 vs	25.78 vs	22.57 s	21.49 s	25.78 s
12.28 w	13.78 w 9.77 w	14.22 w	11.81 w 8.94 w	11.08 w 9.98 w	12.37 w 10.56 w
7.01 m 5.80 m	5.31 w 5.09 w 4.92 w	5.67 w	4.61 m	4.91 w	
4.46 m 4.36 m 4.25 m 4.04 w 3.91 s 3.58 w 3.40 w	4.57 m 4.27 w 4.08 m 3.76 w	4.47 w 4.36 w 4.22 w	4.33 w 4.13 w 3.97 m 3.91 m 3.61 vw 3.50 vw	4.57 w 4.26 w 4.15 w 3.89 w	4.29 w 4.13 w 3.97 w 3.61 vw
				3.46 vw	

pressure because the d spacings of both the low angle reflections are equal. Generally speaking, the high pressure WAXD results correspond well with the main results obtained by high pressure DTA, except for the failure to observe by DTA the monotropic transition of the D_L phase at 300 MPa.

In conclusion, the discotic lamellar phase of C12TPP is found on cooling at high pressures above a critical pressure (240 MPa); the D_L phase appears monotropically in the sequence $I \rightarrow D_L \rightarrow Cr_5 \rightarrow Cr_6$ on cooling, but the sequence is $Cr_6 \rightarrow Cr_5 \rightarrow I$ on heating. Of course, the D_L phase appears reversibly at lower pressures below 240 MPa. Further investigation of the structural behaviour of the various phases of C12TPP is under progress in this laboratory.

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