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Corrigendum

Enantiotropic and monotropic transitions of the discotic mesogen 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrin under pressureYOJI MAEDA*¹ and YO SHIMIZU²¹ National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan² Osaka National Research Institute, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

The authors earlier reported [1] the fact that the enantiotropic liquid crystal transition of the discogen 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrin (C12TPP) at atmospheric pressure changes reversibly to a monotropic transition under hydrostatic pressure. Structural behaviour was studied [2] using a rotating anode X-ray generator equipped with a high pressure vessel on the wide angle goniometer.

Errors in the calculation of the 2θ values have been corrected and the true values for the d spacings differ significantly from those reported in ref [1]. The correct Bragg spacings are given now in the table and used in the figure, which replace the table and figure 7, respectively, in ref [1]. The new results are put in context by the following information.

The X-ray patterns were obtained for the crystal Cr₂ on heating and subsequent cooling at 300 MPa. Crystal Cr₂ was held at temperatures up to 95°C and then the Cr₂-(Cr₄)-Cr₅ transition occurred at about 100°C. The X-ray pattern of crystal Cr₅ was maintained in a wide temperature region between 100°C and 180°C, until the Cr₅-I transition occurred at 183°C. The X-ray pattern of crystal Cr₅ exhibits a strong reflection at $2\theta = 3.77^\circ$ ($d = 23.44 \text{ \AA}$) with several reflections at wide angles different from the D_L phase. The heating experiment at 300 MPa indicates the transformation Cr₂-100°C-Cr₅-183°C-I. In this case, the Cr₄-Cr₃ transition observed as a peak on the DTA curve was not confirmed clearly by the X-ray behaviour. The X-ray patterns of the sample on subsequent cooling from 185°C show a small but sharp reflection at $2\theta = 2.79^\circ$ ($d = 31.64 \text{ \AA}$) in a small temperature region between 150°C and 142°C. This reflection is exactly the same as one given by the D_L phase which is observed reversibly at atmospheric pressure. This represents clear evidence for the monotropic D_L phase which appeared on cooling at 300 MPa.

The cooling experiment at 300 MPa shows the I→D_L transition at about 150°C, followed by the D_L→Cr₅ transition at about 142°C. The X-ray pattern of crystal Cr₅ displays a strong reflection at $2\theta = 3.53^\circ$ ($d = 24.98 \text{ \AA}$) and weak wide angle reflections. Further cooling gives the Cr₅→Cr₆ 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 in the figure. Reheating the sample at 300 MPa showed the Cr₆-Cr₅-I transition.

The table lists the Bragg spacing (d spacing) data calculated from the reflection peaks of the various crystals

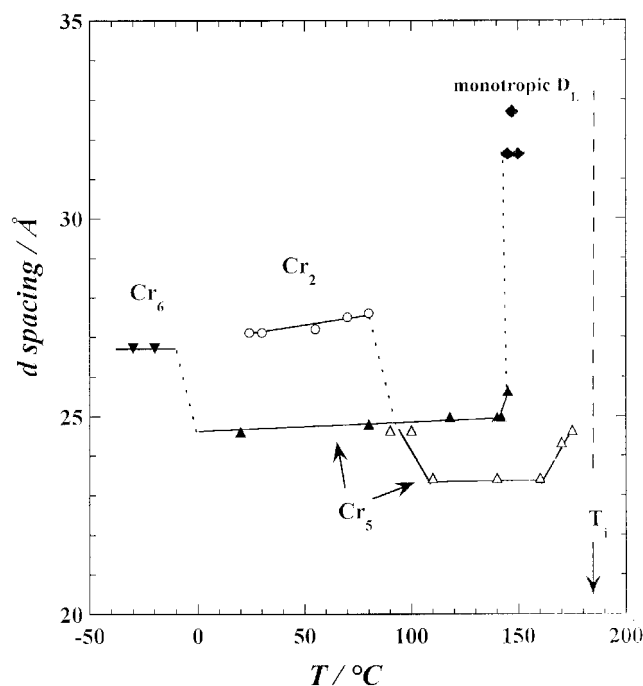


Figure. Temperature dependence of the d spacing of the low angle reflection at 300 MPa. Open and filled symbols relate to measurements made on heating of Cr₂ and subsequent cooling processes, respectively.

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Table. Bragg spacings (Å) of the various crystalline phases and the D_L phase of C12TPP.

Atmospheric pressure			300 MPa		
Cr ₂ (24°C)	Cr ₁ 45°C	D _L 70°C	Cr ₆ – 20°C	Cr ₅ 30°C	monotropic D _L 150°C)
27.92 s	31.64 m 22.34 vs	31.64 vs	26.74 vs	24.98 s	31–32 s
14.17 m	10.92 w	16.09 w	13.56 w 10.05 w	11.11 w	
8.34 w	6.77 w				
7.76 m	5.87 w	6.28 w			
6.34 m	5.62 w	5.43 w			
5.09 w	5.33 w		5.01 m	5.29 w	
4.85 m	4.96 s	4.91 w		4.91 w	
4.71 m		4.77 m			
4.59 m	4.64 m		4.69 w	4.59 w	
4.39 w	4.39 s		4.47 w	4.39 w	
4.24 vs			4.30 m	4.14 w	
			4.22 m		
3.84 w			3.89 w		
			3.77 w	3.73 w	
3.58 w	3.68 w 3.46 w		3.64 vw		

* X-ray data were taken on slow cooling at atmospheric pressure and 300 MPa.

and the D_L phase of C12TPP cooled at atmospheric pressure and 300 MPa. The monotropic D_L phase appears to be the same as the D_L phase observed at atmospheric pressure because the *d* spacing of the low angle reflection is exactly the same. The high pressure WAXD results correspond well with the thermal behaviour observed by high pressure DTA. In conclusion, the discotic phase of C12TPP is observed as a monotropic phase at high pressures above 240 MPa: the D_L phase appears by the I → D_L → Cr₅ → Cr₆ process on cooling, despite the Cr₆ → Cr₅ → I process observed on heating. The D_L

phase usually appears as an enantiotropic phase at low pressures below about 200 MPa. Further investigations on the phase behaviour of C12TPP are under progress in our laboratory.

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