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DSC studies on *p*-cyanophenyl *p*-(*n*-alkyl)benzoate liquid crystals: evidence for polymorphism and conformational change

G.A. Oweimreen*, M.A. Morsy

Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

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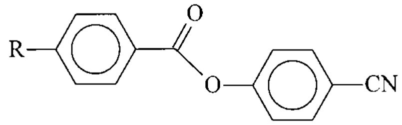
Abstract

Temperatures and enthalpy changes are reported for the melting, clearing, and nematic-to-solid transition of the *p*-cyanophenyl *p*-(*n*-alkyl)benzoate (RCBz) liquid crystals. The results reveal that several solid structures exist for the RCBzs. Evidence that the transitions between the various solid forms involve conformational changes is provided by exotherms and endotherms appearing in heating and cooling cycles, respectively. The study also demonstrates that as long as melted RCBzs are not allowed to solidify they undergo repeated, reversible nematic-to-isotropic and isotropic-to-nematic transitions making them suitable for use in liquid crystal displays (LCD). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Liquid crystals; Polymorphism; Phase transitions; Enthalpies; Conformations

1. Introduction

The electro-optical behavior [1] of the *p*-cyanophenyl *p*-*n*-alkylbenzoates (RCBz, Scheme 1) and their chemical stability makes them suitable for use as components in materials for liquid crystal displays (LCD).



Scheme 1.

From a thermodynamic point of view, the ethyl (2CBz), *n*-propyl (3CBz), *n*-butyl (4CBz), and *n*-pentyl (5CBz) members of the RCBz series are monotropic [1,2]. They melt to an isotropic phase that undergoes an isotropic-to-nematic transition on cooling. Other molecular [3] and polymeric [4] thermotropic liquid crystals are known to exhibit monotropic behavior. The higher members of the RCBz series are enantiotropic [1,2] with mesophases that are thermodynamically stable with respect to both, the isotropic and crystalline phases, within the temperature range from the melting point, ϑ_m, to the clearing-point temperature, ϑ_c.

Several studies on the RCBz series of liquid crystals have been carried out since their synthesis and characterization [1]. Hoffmann–La Roche [5] reported the physical properties of these liquid crystals and their melting and clearing temperatures as obtained using a polarizing microscope. The order parameter for the nematic phase of the heptyl (7CBz) homologue was determined by optical birefringence [6] and X-ray

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*Corresponding author. Fax: +966-3-860-4277; e-mail: ghassan@dkfupm.edu.sa

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diffraction [7]. The crystal structure and molecular packing were also determined for the pentyl (5CBz) [8] and heptyl (7CBz) [7,9] homologues. Bhattacharjee et al. [7] report a solidification temperature, ϑ_s, for 7CBz at a temperature lower than its melting temperature. None of these studies sheds light on the existence of crystalline polymorphs. However, recent electron paramagnetic resonance (EPR) [10,11] and differential scanning calorimetric (DSC) [11] studies on the enantiotropic liquid crystal *p*-(*n*-hexyl)-*p*′-cyanobiphenyl (6CB) and the *n*-hexyl (6CBz) and *n*-heptyl (7CBz) members of the RCBz series indicate that they exhibit ploymorphism in the solid state.

In order to investigate the possible existence of more than one solid structure for the monotropic members of RCBz series, this DSC study was undertaken. In this paper, we report on the solidification and melting behavior of the RCBz liquid crystals. DSC curves measured to as low as −30°C revealed that all the RCBz homologues studied exhibit polymorphism in the solid state. The observed solid–solid modifications are attributable to conformational changes.

2. Experimental

2.1. Materials

The members of the RCBz homologous series of liquid crystals were obtained from Hoffmann–La Roche and used as supplied. Cyclohexane from Fluka (puriss grade) was used as supplied to calibrate the DSC unit.

2.2. Differential Scanning Calorimetry (DSC)

The thermal properties of several members of the RCBz series were studied using a Perkin–Elmer differential scanning calorimeter (DSC-4). Cyclohexane was used for calibration of the temperature and heat of fusion of the DSC unit, as recommended by Perkin–Elmer for measurements using liquid nitrogen as coolant. Empty-pan corrections were carried out for all DSC runs and the temperature calibration using cyclohexane was repeated frequently, particularly when the heating and cooling rates were changed. The independence of the nematic-to-isotropic transition temperature ϑ_{NI} and the isotropic-to-nematic transition temperature ϑ_{IN} of the heating and cooling rates, respectively, constituted evidence of the goodness of the calibrations at the different rates. The temperature of the various transitions and the areas of the endotherms and exotherms, needed to calculate the enthalpy changes at the transitions, were determined using the procedures outlined in the DSC-4 instruction manual.

The masses of the liquid crystal samples were between 4.8 and 7.2 mg. Prior to the DSC runs, each sample was heated to ca. 10°C above its reported [5] melting point and held at that temperature for ca. 2–3 min to ensure its complete transformation to the isotropic phase. Consecutive cooling, heating, then cooling curves were recorded at a rate of 10 K/min between this temperature and −30°C. To investigate the dependence of the different transition temperatures on the heating or cooling rates, heating and cooling curves were obtained at 3 K/min between 0°C and the above mentioned upper temperature. In the case of 6CBz, lowering the heating rate from 10 to 3 K/min or lower accomplished the clear separation of the endotherm for the nematic-to-isotropic transition from the broad melting endotherm that preceded it by 3°C (Fig. 3).

To observe a transition from the nematic phase to the isotropic phase of a monotropic liquid crystal its nematic phase was not allowed to solidify. The liquid crystal was melted, then cooled down to a temperature below its isotropic-to-nematic transition temperature yet above its solidification temperature before heating it to cross its nematic-to-isotropic transition temperature. This experiment was carried out for 2CBz, 3CBz, and 4CBz.

3. Results and discussion

The DSC curves shown in Fig. 1 are for the cooling of the RCBz liquid crystals from temperatures above their melting points down to −30°C at a rate of 10 K/min. Fig. 2 gives the heating runs between the same temperature limits and at the same rate. The onset of the major exotherms in Fig. 1, and the onset of the major endotherms in Fig. 2, show that the temperature at which each of the RCBz liquid crystals solidifies, ϑ_s, is much lower than the temperature at which it melts, ϑ_m. As the Appendix A shows, the ϑ_m values

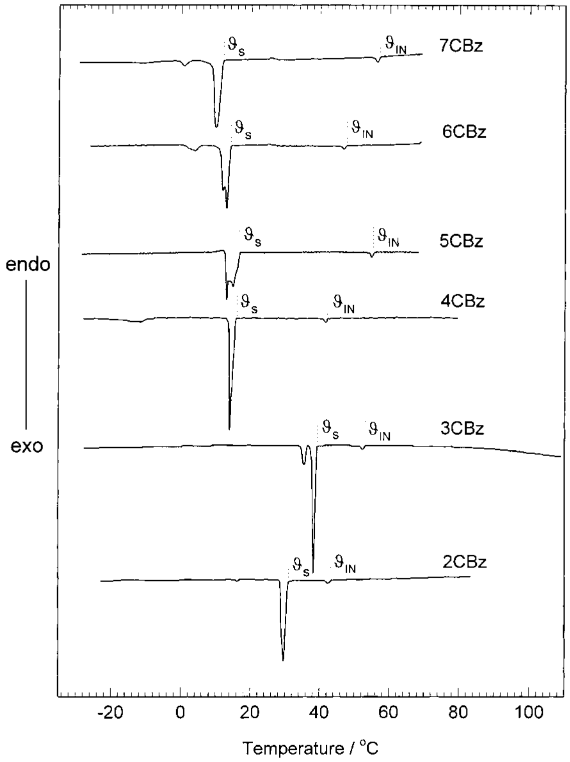

Fig. 1. DSC cooling curves for 2CBz, 3CBz, 4CBz, 5CBz, 6CBz, and 7CBz at the rate of 10 K/min. The vertical dotted lines indicate the onset temperatures in °C for the isotropic-to-nematic transitions, ϑ_{IN}, and nematic-to-solid (solidification) transitions, ϑ_{s}.

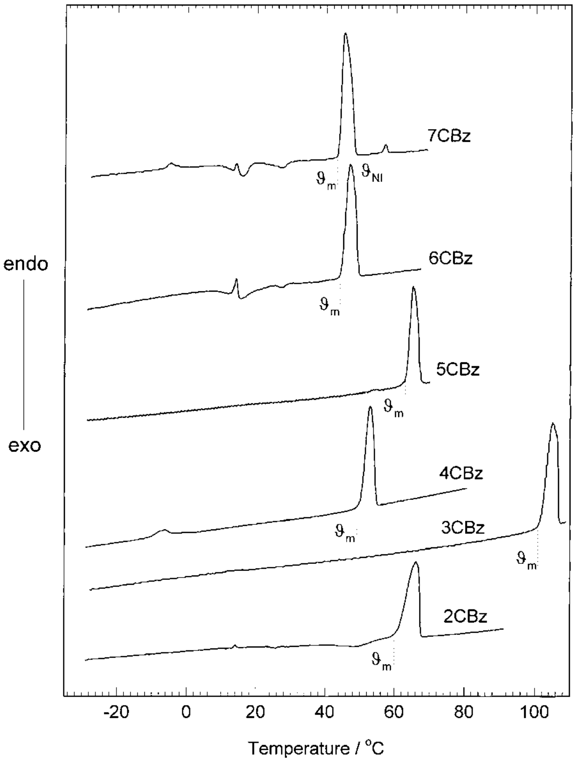

Fig. 2. DSC heating curves for 2CBz, 3CBz, 4CBz, 5CBz, 6CBz, and 7CBz at a rate of 10 K/min. The vertical dotted lines indicate the onset temperatures in °C for the solid-to-nematic/solid-to-isotropic (melting) transitions, ϑ_{m}, and nematic-to-isotropic transitions, ϑ_{NI}.

are practically independent of the heating rate (see Fig. 3(B)) whereas the ϑ_{s} values vary with the cooling rate (see Fig. 3(A)). This, and the difference between ϑ_{s} and ϑ_{m}, suggest that the solid phase of an RCBz liquid crystal exhibits monotropic polymorphism [12]. The ϑ_{s} and ϑ_{m} values averaged over the different cooling and heating rates, respectively, are given in Table 1, which also includes ϑ_{m} values obtained by Hoffmann–La Roche [5] using a polarizing microscope, by Morsy et al. [11] for 6CBz and 7CBz using electron paramagnetic resonance (EPR), and by X-ray diffraction (XRD) for 5CBz [8] and 7CBz [9]. Except for the suspect ϑ_{m} values obtained for 2CBz and 4CBz using the optical microscope, all other values are in good agreement.

The measured curves for 6CBz (Figs. 1 and 3), 7CBz (Figs. 1 and 2), and the monotropic RCBzs (represented by the measured curves for 4CBz in Fig. 4) show that, for each of the RCBz's, the onset temperature for the nematic-to-isotropic transition, ϑ_{NI}, practically coincides with the onset temperature for the isotropic-to-nematic transition, ϑ_{IN}. This coincidence was found to be independent of the cooling and heating rates (see Appendix A). This temperature (at which ϑ_{NI} and ϑ_{IN} coincide), or the average of ϑ_{NI} and ϑ_{IN}, is referred to in this paper as the clearing temperature, ϑ_{c}. The ϑ_{c} values for all the liquid crystals studied are given in Table 1, which also includes ϑ_{c} values obtained by Hoffmann–La Roche [5] using a polarizing microscope and by Morsy et al. [11], for 6CBz and 7CBz, using electron paramagnetic resonance (EPR). The ϑ_{c} values obtained from the different methods (where applicable) are in good agreement.

The results obtained for the nematic-to-isotropic transitions of the monotropic liquid crystals are given

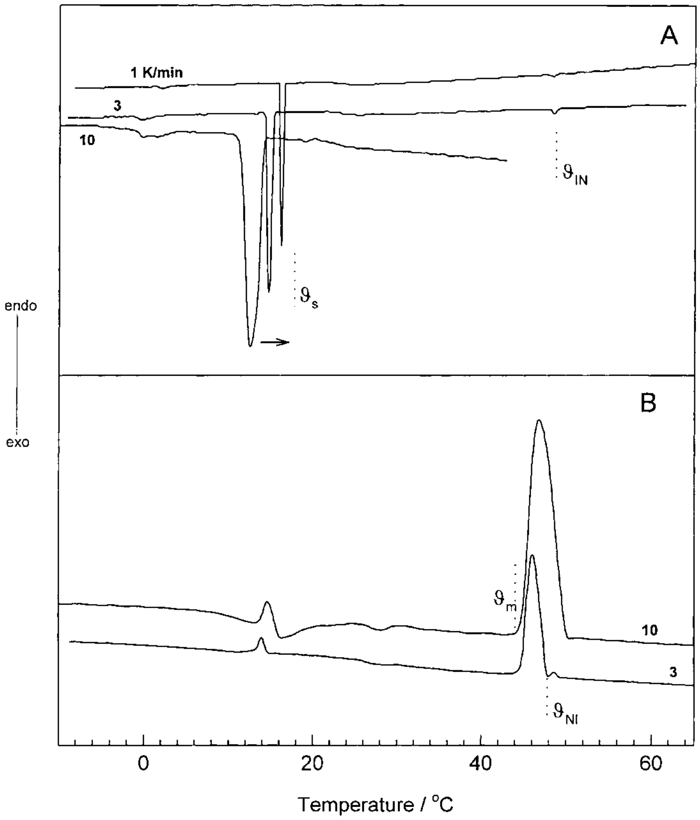

Fig. 3. DSC cooling, A, and heating, B, curves for 6CBz. The numbers on the curves are for heating or cooling rates in K/min and the vertical dotted lines indicate the onset temperatures in °C for the isotropic-to-nematic, ϑ_{IN}, solid-to-nematic (melting), ϑ_m, or nematic-to-solid (solidification), ϑ_s, transitions.

in parentheses in Appendix A. Representative DSC curves are shown for 4CBz in Fig. 4. The results clearly showed that, as long as solidification does not occur, the nematic phase persists for long periods and nematic-to-isotropic and isotropic-to-nematic transitions may be repeatedly obtained in an unlimited number of heating and cooling cycles. Maintaining a temperature above ϑ_s for the monotropic RCBzs after melting them has practical ramifications for their use (with the probable exception of 3CBz which is a solid below 35°C) in LCDs either on their own or with other liquid crystals.

The molar enthalpies of melting ($\Delta_m H$), nematic-to-solid transition ($\Delta_s H$), and transition between nematic and isotropic phases ($\Delta_c H$) obtained from DSC curves at different cooling and heating rates are reported in the Appendix A and their average values are given in Table 1. For each of the liquid crystals studied $\Delta_s H$ is numerically smaller than $\Delta_m H$ and the disparity between their numerical values is much larger than the numerical value of $\Delta_c H$. This provides support for the suggestion that, for all the RCBzs, the structure of the solid phase obtained on solidification of a nematic phase is different from, and less stable than, the structure of the solid phase that exists prior to melting. The existence of several solidification peaks, clearly seen on expansion of the DSC curves as illustrated for 2CBz, 4CBz, and 7CBz in Fig. 5 provides evidence for monotropic polymorphism in the solid phase. The double-headed arrows in parts C and D in Fig. 5 point to an endotherm, preceding solidification on cooling at a temperature that is independent of the cooling rate, which appears as a rate-independent exotherm at the same temperature and precedes

Table 1
Transition temperatures (ϑ in °C) and enthalpies (ΔH in kJ mol^{-1}) for the RCBz liquid crystals. The subscripts s, m, and c refer, respectively, to the nematic-to-solid (solidification), solid-to-nematic/solid-to-isotropic (melting), and nematic-to-isotropic or isotropic-to-nematic (clearing) transitions

Liquid crystal	ϑ_s/°C		$\lvert\Delta H_s\rvert$/ (kJ mol^{-1})	ϑ_m/(°C)		ΔH_m/ (kJ mol^{-1})	ϑ_c/(°C)		$\lvert\Delta H_c\rvert$/ (kJ mol^{-1})
	other studies	DSC		other studies	DSC		other studies	DSC	
2CBz	—	28.2	13.93	75.1 [a]	60.6	25.61	42.6 [a]	40.9	0.389
3CBz	—	36.5	18.62	101.6 [a]	102.9	33.89	53.2 [a]	53.6	0.586
4CBz	—	15.8	18.83	66.5 [a]	49.4	23.60	42.3 [a]	41.4	0.531
5CBz	—	16.5	19.66	60.0 [a] 60.5 [b]	63.0	25.10	56.5 [a]	56.2 56.0 [b]	0.833
6CBz	17.3 [c]	14.5 [d]	18.83	44.5 [a] 45.5 [c]	45.3 [d]	37.03	48.0 [a] 48.8 [c]	48.3 [d]	0.661
7CBz	23.2 [c] ~33 [e]	12.7 [d]	21.76	43.5 [a] 44.3 [c] 43.5 [e]	43.5 [d]	35.48	56.5 [a] 56.4 [c] 56 [e]	56.3 [d]	0.937

[a] Measurements using a polarizing microscope (Ref. [5]).
[b] Measurements using X-ray diffraction (Ref. [8]).
[c] Measurements using electron paramagnetic resonance (Ref. [11]).
[d] Ref. [11].
[e] Measurements using X-ray diffraction (Ref. [9]).

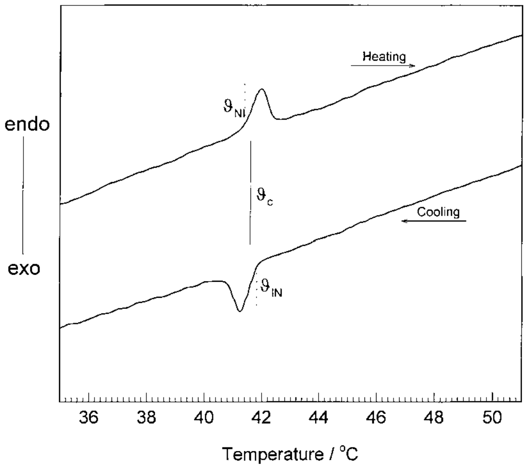

Fig. 4. DSC cooling and heating curves for 4CBz at a rate of 3 K/min. The vertical dotted lines indicate the onset temperatures in °C for the isotropic-to-nematic, ϑ_{IN}, or nematic-to-isotropic, ϑ_{NI}, transitions and the solid vertical line their average temperature, ϑ_c.

melting on heating. This cooling-endotherm/heating-exotherm indicates the existence of conformational changes. Furthermore, the appearance of two small exotherms on heating, one at or just before ϑ_s and the second between ϑ_s and ϑ_m (encircled in parts A and D of Fig. 5 for 2CBz and 7CBz, respectively), which are dependent on the heating rate (seen on careful contrast of the heating runs in parts C and D of Fig. 5 for 7CBz), provide additional proof that solid–solid conformational changes occur as the most stable solid form is approached. These exotherms are far too broad to be clearly distinguished in the cases of 3CBz, 4CBz, and 5CBz (see part B of Fig. 5 for 4CBz where the onset of a dip in the DSC curve is indicated with an ellipse).

As mentioned earlier, the relation:

$$\Delta_m H > (|\Delta_s H| + |\Delta_c H|)$$

holds for all the RCBz liquid crystals studied. An examination of the data in the Appendix A shows that the difference between $\Delta_m H$ and ($|\Delta_s H|+|\Delta_c H|$) is much larger than the propagated uncertainties in $\Delta_m H$, $\Delta_s H$ and $\Delta_c H$. In addition, it has been found throughout that:

$$\Delta_m H - (|\Delta_s H| + |\Delta_c H|) > \sum \Delta_{ss} H$$

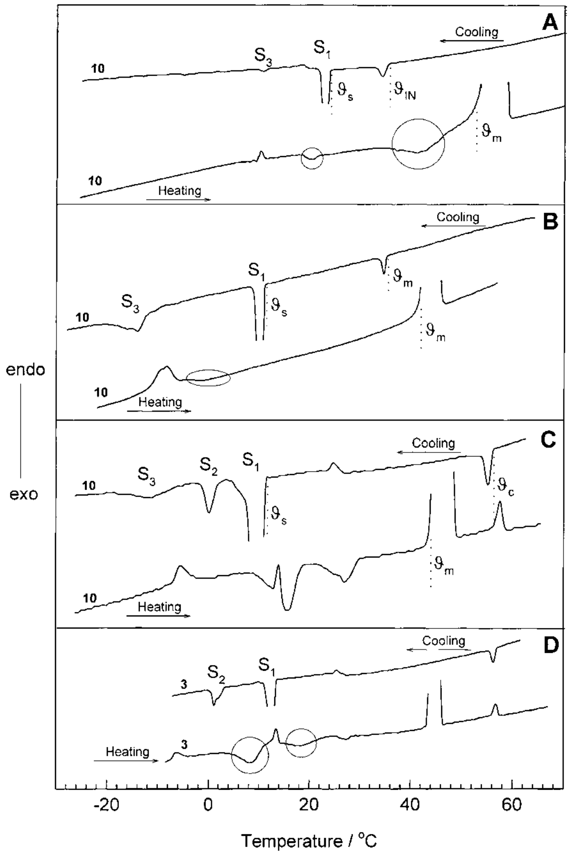

Fig. 5. Expanded DSC cooling and heating curves for 2CBz, A, 4CBz, B, and 7CBz, C, at a rate of 10 K/min and for 7CBz, D, at a rate of 3 K/min. The nematic-to-solid exotherm (S_1) and the melting endotherm are truncated. Other solidification exotherms (S_2 and S_3) and their corresponding endotherms are identifiable. The DSC curves also show endotherms and exotherms in cooling and heating cycles, respectively.

where $\sum\Delta_{ss}H$ refers to the sum of enthalpy changes of all other solid–solid transformations. The endotherm appearing in the vicinity of ϑ_s between the two encircled exotherms in the heating runs for 7CBz (in part D of Fig. 5) and appearing within a broad exotherm (in part C of Fig. 5) indicates that some solid structure is undergoing changes as a result of heat absorption while other solid–solid transformations lead to a release of heat. This leads us to conclude that a mixture of different distinct solid forms involving varying amounts of the sample transforms to one solid form prior to melting.

4. Conclusion

Accurate temperatures and enthalpy changes for the melting and clearing transitions and the main solidification transition were obtained for the RCBz liquid crystals. Disparities between ϑ_m and ϑ_s, the melting and main solidification temperatures, respectively, and $\Delta_m H$ and $\Delta_s H$, the enthalpies of the corresponding transitions, indicate that the structure of the solid existing just before melting is different from that which is obtained when the nematic phase just solidifies. Expansion of the DSC curves revealed the existence of transitions between different solid forms. Evidence that the transitions between these solid forms involve molecular conformational changes is provided by exotherms and endotherms showing up in heating and cooling DSC curves, respectively. Clearly, on heating, several distinct solid forms transform into each other until the most stable form that melts at ϑ_m is reached.

This study demonstrated that reversible nematic-to-isotropic and isotropic-to-nematic transitions are repeatedly obtained for melted monotropic RCBz liquid crystals that are not allowed to cool below the solidification temperature ϑ_s. This makes them suitable for use in LCDs.

Acknowledgements

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Appendix A

Transition temperatures (ϑ in °C) and enthalpies (ΔH in kJ mol^{-1}) from DSC curves for the RCBz liquid crystals using different cooling and heating rates. The subscripts s, m, and c refer, respectively, to the nematic-to-solid (solidification), solid-to-nematic (melting), and nematic-to-isotropic or isotropic-to-nematic (clearing) transitions

Liquid crystal	Scan rate/(K min^{-1})	Cycle	Type of transitions					
			solidification		melting		clearing	
			ϑ_s/(°C)	ΔH_s/(kJ mol^{-1})	ϑ_m/(°C)	ΔH_m/(kJmol^{-1})	ϑ_c/(°C)	ΔH_c/(kJmol^{-1})
2CBz	10	cooling	28.6	−14.64	—	—	41.0	−0.402
		heating	—	—	60.2	25.06	—	—
		cooling	29.2	−11.88	—	—	41.0	−0.356
	3	heating	—	—	61.0	26.15	(39.9) [a]	(0.314) [a]
		cooling	26.9	−15.40	—	—	41.6	−0.485
3CBz	10	cooling	38.2	−21.00	—	—	52.3	−0.623
		heating	—	—	102.2	33.76	—	—
		cooling	36.2	−16.57	—	—	52.8	−0.598
	3	heating	—	—	103.5	34.02	(54.1) [a]	(0.498) [a]
		cooling	35.2	−18.20	—	—	55.1	−0.623
4CBz	10	cooling	14.6	−18.58	—	—	41.5	−0.548
		heating	—	—	49.5	23.64	—	—
		cooling	17.0	−18.87	—	—	41.2	−0.540
	3	heating	—	—	49.3	23.60	(41.3) [a]	(0.477) [a]
		cooling	15.9	−18.95	—	—	41.6	−0.561
5CBz	10	cooling	13.7	−19.16	—	—	55.7	−0.895
		heating	—	—	63.1	25.19	—	—
		cooling	18.9	−20.13	—	—	56.2	−0.761
	3	heating	—	—	62.8	24.98	—	—
		cooling	17.0	−19.75	—	—	56.7	−0.837
6CBz	10	cooling	13.6	−18.45	—	—	47.5	−0.657
		heating	—	—	45.5	36.78 [b]	masked peak	
		cooling	14.5	−18.37	—	—	48.1	−0.695
	3	heating	—	—	45.4	36.15 [c]	48.3	0.460 [c]
		cooling	15.5	−18.62	—	—	48.7	−0.644
	1	cooling	16.5	−20.25	—	—	48.8	−0.644
7CBz	10	cooling	11.1	−21.67	—	—	56.2	−1.021
		heating	—	—	43.7	35.61	56.4	0.954
		cooling	10.3	−21.71	—	—	56.3	−1.050
	3	heating	—	—	43.4	35.19	56.1	0.808
		cooling	13.2	−21.92	—	—	56.6	−0.849

[a] These values were obtained from DSC curves of nematic phases that were not allowed to solidify.

[b] This value is obtained by subtracting the average of the $\Delta_c H$ values obtained from the cooling runs from the ΔH value obtained for the broad peak that included the melting and the nematic-to-isotropic transitions.

[c] A large error is associated with these values owing to the overlap between the broad melting peak and the peak for the nematic-to-isotropic transition.

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