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Dilatometry of the discotic mesogen 2,3,6,7,10,11-hexa-*n*-octanoyloxytriphenylene (HAT-C8)

An anomalous columnar–isotropic phase transition

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The title compound HAT-C8 exhibits a columnar to isotropic phase transition at 402·16 K. Dilatometric studies of pure HAT-C8 as a function of temperature show the higher temperature isotropic phase to be denser than the lower temperature columnar mesophase. The fractional volume change is similar to that observed for benzene hexa-*n*-alkanoates, but of opposite sign. Such anomalous density changes are rare. Since the columnar–isotropic transition entropy has been measured, dp/dT has been estimated from the Clapeyron equation.

1. Introduction

From our earlier dilatometric study of the benzene-hexa-*n*-alkanoates BH7 and BH8, i.e. the heptyl and octyl derivatives, we found very little difference between the sign of magnitude of the fractional volume change occurring at the columnar to isotropic phase transition and that occurring at a typical nematic to isotropic phase transition [1–5]. This disagreed with a theory that predicted a fractional volume change ten times larger than was observed [6, 7]. Since our study of BH*n* compounds, many new discotic mesogens that exhibit a variety of organization of the disc-shaped molecules in the columnar phases have been discovered and characterized [8, 9]. In particular, columnar phases are now known to consist of rectangularly packed columns. The title compound 2,3,6,7,10,11-hexa-*n*-octanoyloxytriphenylene, herein called HAT-C8, was one of the first mesogens shown to exhibit rectangular column packing [10, 11]. The BH*n* compounds of our earlier study exhibit hexagonal column packing. Our motivation to undertake this study was to discover how the structure of the columnar phase influences the volume discontinuity at the columnar–isotropic phase transition.

2. Experimental

The HAT-C8 was the same sample used in the heat capacity studies reported earlier [12]. The columnar to isotropic transition temperature for that sample was 402·16 K. The molecular weight of HAT-C8 is 1·08148 kg mol^{-1}. The volume changes associated with the extensive solid state polymorphisms were not studied here. The density measurements are made using a Lipkin bicapillary pycnometer, following the general technique described in the ASTM Method D1481-62. The pycnometer was made from one piece of precision bore capillary that had a sample chamber formed in it by blowing a bubble in the capillary tube. Once the sample chamber was formed, the piece was bent into a U-shape and a fiducial mark scratched on the capillary about 1 cm above the sample chamber. By controlling the size of the bubble, pycnometers of various total

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capacities could be easily constructed. The pycnometer used had a volume of about 2 ml. The actual weight of HAT-C8 in the pycnometer was 2·5438 g. The liquid heights in the pycnometer were measured using a cathetometer. The precision of the total heights measurement was generally ±0·010 cm. The temperature studies were performed by immersing the pychometer in a Neslab Tamson Model TXK 40 bath filled with Dow Corning 200 heat transfer fluid. The temperature was controlled on average to within ±7 mK and measured with a Hewlett–Packard Model 2804A Quartz thermometer. The pycnometer was calibrated using freshly boiled, deionized water and freshly distilled *n*-butylbenzene. Even though the water calibration data had to be extrapolated for this application since the temperature range of interest involved the columnar–isotropic transition at 402·16 K, the water calibration data give the more consistent, meaningful results. The water density data used for the calibration was taken from [13]. The calibration data were inserted into the equation

$$\text{pycnometer volume/ml} = 1{\cdot}4666 \times 10^{-3}T + 1{\cdot}0721 \times 10^{-3}(h\text{-}18{\cdot}1) + 2{\cdot}5425 \times 10^{-4}Th + 2{\cdot}4584.$$

Here T is the sample temperature in °C and h is the sum of the two individual capillary heights of the sample in the pycnometer each measured in cm from the fiducial mark.

It should be noted that the columnar phase of HAT-C8, is quite viscous. The high viscosity of the columnar phase meant the only practical volume measurements depended on always beginning measurements on cooling from the isotropic phase. The isotropic phase routinely supercoooled about 2°C below the equilibrium columnar–isotropic phase change temperature before spontaneously transforming into the columnar phase. The cooling procedure involved lowering the set-point temperature of the oil bath by about 0·3°C and waiting for equilibrium to be established. Generally equilibrium was achieved in about one hour. Once the columnar phase was obtained, it could be further cooled. Experimentally, again because of the viscosity of the columnar phase, the extent of cooling could not be very large before noticeable void regions appeared in the capillaries indicating the loss of temperature-flow equilibrium. If a non-equilibrium state was obtained, the sample could be reheated to the isotropic phase and repeatedly supercooled through the phase transition, always with the observation of an increase in molar volume for the columnar phase. While several qualitative trials of this nature were conducted, the quantitative data, discussed in Section 4 was obtained during a single cooling, during which time all reasonable precautions were taken to assure equilibrium was maintained. Of course, eventually at low enough temperature, the viscosity became so great that void formation was observed and no additional waiting, even for about one day, was sufficient for the gravitional flow to destroy the void. Additional confirmatory evidence for the anomalous density change was sought by looking for the change in the equilibrium phase change temperature as a function of pressure. Given the pressure ranges possible with the available equipment, vacuum to 1 bar over pressure, the change in the D–I equilibrium temperature was suggestive of a negative value for dp/dT, but not conclusive.

In addition to the pycnometer measurements, the thermal expansion behaviour of a sample contained in a precision flat bore capillary tube was observed with a polarizing microscope equipped with a hot stage. An Olympus BH-2 polarizing microscope equipped with a Mettler FP52 hot stage and FP5 controller was used. The precision flat bore capillary tube was obtained from Vitro Dynamics, Rockaway, N.J. It should be noted that the rates of temperature change in these experiments were much faster than in the case of the pycnometer measurements.

3. Results

The basic results of the experiment are contained in figures 1 and 2. Figure 1 presents the molar volume of HAT-C8 as a function of temperature using the water calibration. The solid lines in both figures are linear regression fits to the data. The volume discontinuity at the transition temperature $T_{NI} = 402{\cdot}16$ K in each case has been obtained by extrapolation of the regression lines. Figure 2 presents the results of observing a length of a fixed mass of sample contained in a precision flat bore capillary tube as a function of temperature. Here we note the length is proportional to the volume of the fixed mass of sample.

The table presents the quantitative results of this experiment and lists for comparison and discussion selected results for similar experiments with different materials. The BH8 compound also exhibits a columnar phase, while PAA, EOAB, and 8CB are classic nematogenic materials. The dramatic observation is that while the orders of magnitude of the fractional volume change are all about the same order, different only by factors of two to four the sign of the change for HAT-C8 is negative. The dp/dT coefficient exhibits the greatest variation in magnitude and sign. Some comments on how the dp/dT were obtained are required. For HAT-C8, dp/dT was calculated using the Clapeyron equation since the transition entropy had been determined earlier [12] and the volume discontinuity was available from this work. The dp/dT value for BH8 was estimated from the p–T graph of Chandrasekhar *et al.* [14]. To estimate dp/dT for 8CB required estimating a value for the transition enthalpy using similar compounds. Both of the discotic mesogens have much larger dp/dT

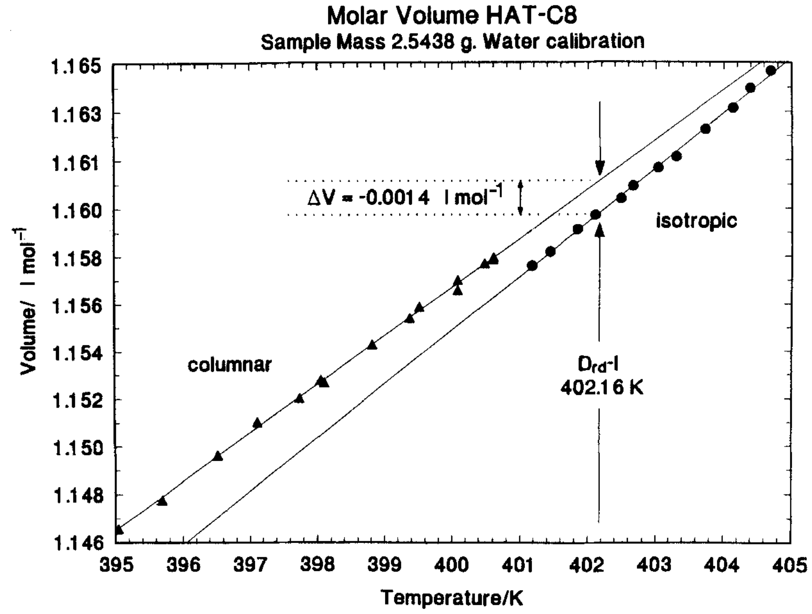

Figure 1. The molar volume ($\mathrm{l\,mol^{-1}}$) as a function of temperature for 2,3,6,7,10,11-hexa-*n*-octanoyloxytriphenylene in the region of the columnar–isotropic phase transition at 402·16 K. The molar volume was obtained using water to calibrate the pycnometer. The uncertainties associated with the measurements are essentially the size of the solid dots marking the data points. The solid lines are linear regression fits to the data of each phase. The mass of the sample was 2·5438 g.

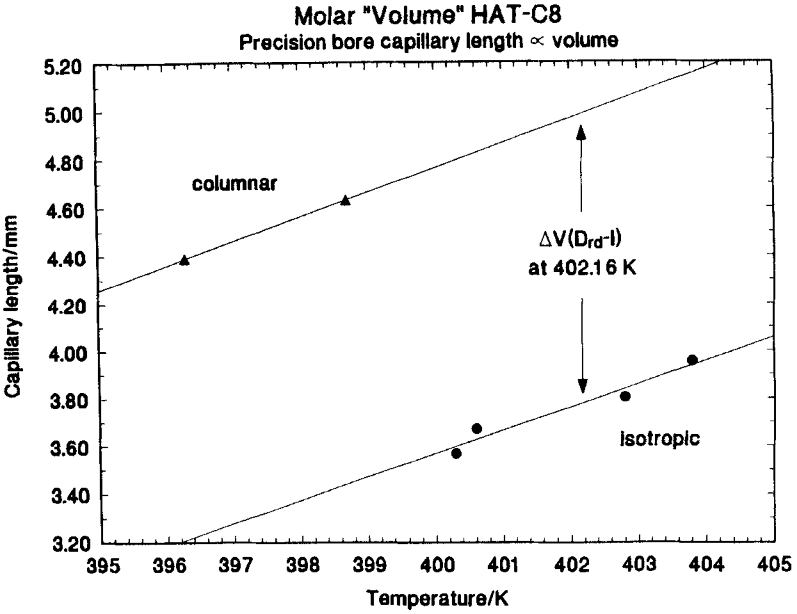

Figure 2. The length of a column of 2,3,6,7,10,11-hexa-*n*-octanoyloxytriphenylene contained in a precision flat bore capillary tube as a function of temperature near the columnar–isotropic phase transition at 402·16 K. The length of the sample in the capillary is proportional to the volume of the fixed sample mass. The solid lines are linear regression fits to the data in each phase. (Of course, such treatment is not necessary for the columnar phase.)

Fractional volume changes and dp/dT at the columnar or nematic to isotropic phase transition for selected mesogens.

Compound	Fractional volume change ($\Delta V/V_n$)/(10^{-3})	(dp/dT)/(atm. K^{-1})
HAT-C8(a) (D_{rd}–I transition)	−1·2	−65
BH8(b) (D_{hd}–I transition)	6·4(c)	170(d)
PAA(e) (N–I transition)	2·8(f)	19(f)
EOAB(g) (N–I transition)	3·3(h)	23(h)
8CB(i) (N–I transition)	1·7(j)	3(k)

(*a*) 2,3,6,7,10,11-Hexa-*n*-octanoyloxytriphenylene, this work.
(*b*) Benzene-hexa-*n*-octanoate.
(*c*) From [1].
(*d*) Estimated from graphical *p*–*T* data [14].
(*e*) *P*-azoxyanisole.
(*f*) From [4].
(*g*) 4-Ethoxy-4′-*n*-octanoyloxyazobenzene.
(*h*) Unpublished results, L. J. Theodore and G. R. Van Hecke.
(*i*) *n*-Octylcyanobiphenyl.
(*j*) From [3].
(*k*) Estimated from volume data in [3] and assumed from ΔH(N–I) = 12 cal. mol^{-1}.

values than the nematic mesogens. This can be understood by noting that the transition entropies for the columnar–isotropic transition are significantly larger than the typical nematic–istoropic values [12, 15]. The significantly smaller dp/dT value for 8CB is noteworthy, which is due to the very small nematic–isotropic transition entropy. (This is, of course, dependent on the validity of the estimated value for the transition enthalpy.) Effectively, the magnitude of dp/dT is determined by the transition entropy while the sign is determined by the volume discontinuity.

The conclusion from each graph is unmistakable. The molar volume of HAT-C8 decreases on going from the lower temperature columnar phase to the higher temperature isotropic phase. The quite different extents of supercooling between the pycnometer and microscope experiments more than likely results from the markedly different cooling rates in the two experiments. That the density of the higher temperature phase is greater in magnitude than the lower temperature phase is a rarely observed phenomenon in any material. We believe this to be the first such observation for liquid crystals, certainly for discotic materials [16].

4. Discussion

The microscopic structures of columnar phases formed by the discotic mesogens BH8 and HAT-C8 have been extensively studied by a variety of methods but most profitably by X-ray diffraction [10, 11]. The structure of the columnar phase of BH8 is described as hexagonal due to the arrangement of the columns of the disc-shaped molecules but disordered with respect to the spacing of the discs within a column. One classification scheme proposes the symbol D_{hd} to denote this columnar mesophase. The structure of HAT-C8 on the other hand is a slight distortion of the hexagonal column arrangement and has, instead, rectangular packing of the columns. The molecular distance between the disc-like molecules is also disordered. The notation for this phase is D_{rd} [8]. An explanation of the anomalous density change may be found in this difference in column packing. If it is supposed that the volume per molecule in the hexagonal packing is a minimum, in effect two dimensional cubic closest packing, then transforming to the isotropic phase from this close packed phase should occur with an increase in the volume per molecule, that is, a decrease in the density of the higher temperature phase. If it is noted that the rectangular packing of columns is not as efficient as hexagonal, the volume per molecule is larger. To explain the anomalous density change, all that is required to understand is that the volume per molecule in the loose rectangular packing is larger than that possible when all structural organization of the columnar phase is lost, that is, in the isotropic phase, the volume per molecule decreases.

The sign and magnitude of the volume change also seems reasonable in light of the calorimetric results available for these two discotic materials. For BH8 and HAT-C8 the heat capacity measurements imply a considerable amount of alkyl chain melting occurring before the actual columnar–isotropic transition. It is noted that for BH8 the heat capacity of the columnar phase is significantly smaller than either the crystalline or isotropic phases that are adjacent to it [13]. The same is true for HAT-C8 except the discrepancy is much smaller [12]. The relatively smaller heat capacity for HAT-C8 could be understood by noting that if the chain melting has occurred, few ways remain for the columns to utilize more heat energy since the columns are constrained to maintain the macroscopic phase organization. Thus in the case of BH8, the large change in heat capacity on going from the columnar phase to the isotropic phase is associated with a large increase in volume per molecule. The smaller change in heat capacity for the columnar–isotropic transition for HAT-C8 is concomitant with the decrease of the volume per molecule. What is not understood is whether this change is due to a chain length effect, that only works for the octyl chain length and rectangular packing, or a general result for any columnar phase with rectangular packing. Since other homologs of HAT-C8 have not been studied, this question remains unanswered.

Often the nematic–isotropic volume discontinuity is characterized by some sort of pre-transitional effect, observed either on cooling the isotropic phase or heating the nematic phase. The BH7 and BH8 discotic mesogens also exhibited quite marked pre-transitional behaviour when heating their D_{hd} columnar phases through to the isotropic phase. If any pre-transitional effects were to occur in the D_{rd} phase of HAT-C8, they would be expected to curiously curve downward rather than the typical upward. However, the lack of data in what would be the pre-transitional region precludes making any meaningful comments about the nature of any pre-transitional effects in HAT-C8.

5. Conclusion

The molar volume of 2,3,6,7,10,11-hexa-*n*-octanoyloxytriphenylene has been measured as a function of temperature. The results show that the molar volume of the columnar phase is larger than that of the higher temperature isotropic phase and consequently dp/dT for HAT-C8 is negative. Moreover, it appears that the magnitude of dp/dT is determined by the transition entropy while the sign is determined by the volume discontinuity. While this anomalous density behaviour can be correlated with the rectangular lattice packing of the columnar phase, it is not known, although suggested here, that the behaviour is general for all discotic mesogens that exhibit rectangular columnar phases.

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