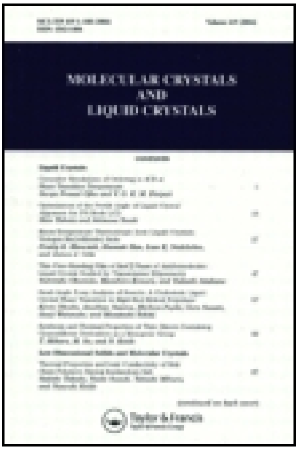

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Thomas H. Smith [a] & Gerald R. Van Hecke [a]

[a] Department of Chemistry, Harvey Mudd College, Claremont, California, 91711, U.S.A.

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Dilatometric Studies on Columnar Mesogens: Benzene Hexa-*n*-Alkanoates†

THOMAS H. SMITH and GERALD R. VAN HECKE
Department of Chemistry, Harvey Mudd College, Claremont, California 91711 U.S.A.

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Molar volume-temperature studies are reported for two disc-shaped molecules exhibiting columnar mesophases: benzene hexa-*n*-heptanoate and hexa-*n*-octanoate. The fractional volume changes observed at the columnar mesophase/isotropic transition are the same order of magnitude as those observed for typical nematic mesophases in disagreement with theoretical model predictions.

INTRODUCTION

The recent discovery that disc-shaped molecules exhibit mesophases initiated great interest not only in the synthesis of new disc molecules with mesomorphic properties but also in the determination of physical and thermodynamic properties of these mesophases.[1-4] Theoretical models have been proposed to understand the existence of these new mesophases.[5,6] One pertinent test of the theories would be to compare the predicted and experimental fractional volume change associated with the isotropic/mesophase transition. The present study was undertaken to test the theoretical predictions and provide such fundamental data. We report here the molar volume-temperature data obtained for two homologs: benzene hexa-*n*-heptanoate, -*n*-octanoate and comment on the magnitude of the fractional volume change occurring at this columnar mesophase/isotropic transition.

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EXPERIMENTAL

The compounds were synthesized by condensing the appropriate *n*-alkanoyl chloride with hexa-hydroxybenzene via the procedure of Neifert and Bartow as recently described by Chandrasekhar *et al.*[7,1a] The hexa-hydroxybenzene was synthesized starting from glyoxal via the procedure of Fatiadi and Sager.[8] This procedure, while giving low yields of the desired hexa-hydroxybenzene product, was found more convenient than the procedure of Neifert and Bartow starting from *i*-inositol.[7] The resultant hexa-esters were purified by multiple recrystallizations from absolute ethanol.

Details of the optical microscopy and differential scanning calorimetry procedures have been described earlier.[9] The dilatometric results were obtained using Lipkin bicapillary pcynometers following the ASTM Method D 1481-62. It should be noted that this ASTM technique is only suitable for density measurements on fluid phases, and, therefore, no data was obtained for the crystal to mesophase transition. The thermostat used was a Neslab Model TXK whose temperature control during these experiments was generally ±5 mK. A Hewlett-Packard Model 2804 A Quartz Thermometer was used to measure the temperature.

RESULTS AND DISCUSSION

Molar volume-temperature data for the heptanoate and octanoate homologs is plotted in Figure 1 and presented in Table 1. The phase transition temperatures are in good agreement with those reported as seen in Table 2. The nonanoate homolog was also synthesized but it was not possible to maintain its metastable mesophase long enough to make suitable density measurements. Both the heptanoate and octanoate homologs exhibit mesophases that readily super-cool with respect to the crystalline phase and the lower temperature points were obtained on the super-cooled mesophase.

In Table 2 is a summary of the volume data in terms of the fractional volume changes $\Delta\bar{V}/\bar{V}_{Iso}$ associated with the mesophase/isotropic transition calculated in two ways: 1. Extrapolation of the linear portion of the mesophase data will define $\bar{V}_M$ and $\Delta\bar{V} = \bar{V}_M - \bar{V}_{Iso}$ at T_{I-M}. $\Delta\bar{V}/\bar{V}_{Iso}$ follows simply thereafter. 2. Calculation of $\Delta\bar{V}$ from Clausius-Clapeyron equation since enthalpy, temperature and dP/dT (from P-T phase diagrams) data are available for these compounds. With respect to the magnitudes calculated by the two procedures, the linear extrapolation yields a maximum value for $\Delta\bar{V}/\bar{V}_{Iso}$ with only questionable thermodynamic meaning. The fractional volumes calculated by the Clausius-Clapeyron equation have thermodynamic meaning but depend on determination of the enthalpy which may have considerable uncertainty associated with its value because of pre-transitional effects. It is

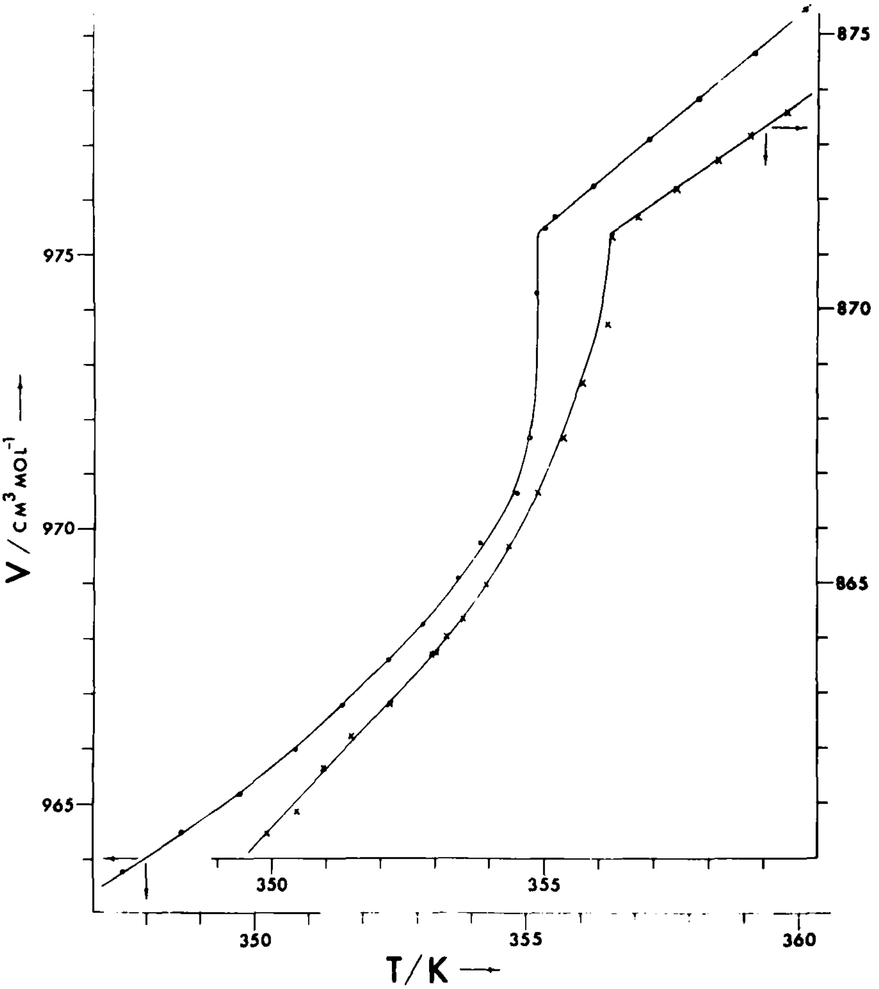

FIGURE 1 Molar volume versus temperature for benzene hexa-*n*-heptanoate X and -hexa-*n*-octanoate O.

quite consistent, however, that the volume changes calculated via the Clausius-Clapeyron equation are smaller than the values obtained by extrapolation.

Either calculation of fractional volumes yields magnitudes on the order 3-4 × 10^{-3} which is the same order of magnitude as observed for nematic/isotropic phase transitions.[10-12] For comparison the value for *p*-azoxyanisole (PAA) is included in Table 2. Such magnitudes are in considerable disagreement with the theoretical calculations which suggest that the volume change should be one or two orders of magnitude greater than these reported here. Gelbart's theory correctly suggests that the enthalpies of the disc meso-

TABLE I

Molar volume versus temperature data in columnar mesophase and isotropic phase for the homologs benzene hexa-heptanoate and benzene hexa-octanoate. Isotropic phase data are indicated with an asterisk*.

Heptanoate		Octanoate	
$\frac{T}{K}$ (±0.005)	$\bar{V}$ / $\mathrm{cm^3 mol^{-1}}$ (±0.25)	$\frac{T}{K}$ (±0.005)	$\bar{V}$ / $\mathrm{cm^3 mol^{-1}}$ (±0.25)
376.262*	885.41	364.638*	983.15
375.706*	885.13	363.795*	982.48
374.336*	883.93	363.004*	981.76
375.303*	883.20	362.058*	980.96
372.191*	882.30	361.150*	980.20
371.299*	881.72	360.166*	979.40
370.492*	881.10	359.225*	978.60
369.400*	880.40	358.204*	977.80
368.408*	879.81	357.293*	977.04
367.359*	879.15	356.273*	976.20
366.481*	878.53	355.348*	975.44
365.452*	877.68	355.543*	975.65
364.471*	877.02	355.208*	974.28
363.400*	876.32	355.082	971.63
362.816*	876.00	354.837	970.63
362.405*	875.77	354.169	969.71
361.918*	875.15	353.755	969.09
361.262*	874.65	353.106	968.25
360.669*	874.41	352.476	967.62
360.050*	874.02	351.619	966.78
359.418*	873.59	350.750	965.98
358.734*	873.13	349.714	965.18
358.174*	872.70	348.652	964.46
357.413*	872.20	347.572	963.74
356.681*	871.65	346.404	962.85
356.206*	871.30	345.236	962.05
356.140	869.70	344.275	961.57
355.696	868.63		
355.337	867.63		
354.863	866.64		
354.359	865.68		
353.945	864.98		
353.508	864.33		
353.219	864.02		
353.041	863.75		
352.948	863.71		
352.178	862.79		
351.470	862.21		
350.965	861.36		
350.481	860.86		
349.884	860.43		

TABLE II

Molar volume and fractional volume changes determined at the temperature corresponding to the first observation of columnar mesophase in the presence of isotropic phase for benzene hexa-*n*-heptanoate and hexa-*n*-octanoate.

Compound	$\frac{V_{\text{Isotropic}}}{\text{cm}^3\text{mol}^{-1}}$ [a]	$\frac{\left(\frac{\Delta \bar{V}}{V_I}\right)}{10^{-3}}$	$\frac{\Delta V}{\text{cm}^3\text{mol}^{-1}}$ [b]	$\frac{\left(\frac{\Delta \bar{V}}{V_I}\right)}{10^{-3}}$	$\frac{T_{I-M}}{K}$
Heptanoate	871.36	4.9	4.1	4.7	356.2 (356.7)[c]
Octanoate	975.35	6.4	3.5	3.6	355.3 (355.0)[c]
PAA		3.5[d]			

[a] Determined at temperature isotropic to first appearance of mesophase.

[b] Calculated from Clausius-Clapeyron equation $\Delta V = \Delta H / T(dP/dT)$ data $\Delta H, dP/dT$ from Ref. 1b.

[c] Data from Ref. 1b.

[d] Data from Ref. 10.

phase/isotropic transition should be larger by an order of magnitude or so than those for typical nematic/isotropic transition.[5] Perhaps it is somewhat surprising, therefore, that the volume data are in such disagreement. However, the following argument provides a possible qualitative explanation of these results. The mesophase exhibited by these hexa-esters is described as columns of stacked disc-like molecules with the columns then arranged in some manner, probably hexagonally. Compared to an ordinary nematic phase which consists of rod-like molecules with their long axis more or less pointing along an average direction, these columnar phases require not just one stage of organization as in the nematic, pointing in the same direction, but two stages: stacking of discs into a column and the resulting columns organizing into some array. Energetically therefore, it should not be surprising that the enthalpy/entropy differences between the columnar mesophase and the isotropic phase is larger than in the nematic/isotropic case. Moreover, the small volume change might be explained by noting that in terms of molecular arrangements, to pass from the columnar phase to isotropic, all that is required is for the discs to slip by one another in such a manner as to lose the orientational order of the columnar phase and produce the random arrangements characteristic of the isotropic phase. This presumably occurs with very little overall volume change but the large energy and entropy changes mentioned.

The richness of mesomorphism exhibited by disc-shaped molecules is only just beginning to be explored. The possibility exists that for some other mesophase exhibited by disc molecules, for example, the rectangular rather than hexagonal mesophase, the fractional volume changes will be quite large. Further comments await experiment.

CONCLUSION

The molar-volume-temperature data as well as the fractional volume changes observed for the columnar mesophase exhibited by these benzene hexa-*n*-alkanoates is typical of results observed for nematic mesophase, and, indeed, this columnar phase, in terms of its volume-temperature behavior, acts as if it were a nematic phase.

Acknowledgments

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