

# Vapor Pressure and Density of Thermotropic Liquid Crystals: MBBA, 5CB, and Novel Fluorinated Mesogens

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The vapor pressures and densities of six thermotropic liquid crystal-forming molecules (mesogens) have been determined experimentally as functions of temperature. The ubiquitous mesogenic compounds *n*-(4-methoxybenzylidene)-4-butaniline (MBBA) and 4'-cyano-4-*n*-pentylbiphenyl (5CB), which both exhibit room-temperature nematic phases, are examined in this study, as are a number of trifluorinated bicyclohexyl and cyclohexylbiphenyl derivatives which find modern use in display applications. Although thermotropic mesogens are of prime importance in modern optoelectronic technologies, there is a scarcity of reliable saturation pressure data for such systems. An apparatus suitable for measurements of vapor pressures between 0.1 and 1333 Pa in the temperature range 298–523 K has been constructed. The adequacy of the apparatus has been verified by measurements on *n*-hexadecane at temperatures between 304 and 372 K, corresponding to vapor pressures between 0.4 and approximately 100 Pa. To our knowledge, our measurements represent the first reliable data for the saturation pressure of the fluid phase of these types of thermotropic compounds; we show that existing data for MBBA is thermodynamically inconsistent. The densities of the fluid phases of these compounds are also measured by means of a glass pycnometer at temperatures between 293 and 368 K.

## 1. Introduction

Liquid crystals are intermediate states of matter (mesophases) between the isotropic liquid and the crystalline solid.<sup>1–3</sup> Mesophases exhibit some of the mechanical properties of a liquid (they have a high fluidity, are unable support shear, form droplets of fluid, and take the shape of the container) but also display anisotropic properties characteristic of a solid (the optical, electrical, and magnetic properties depend on the orientation of the sample). It is the underlying anisotropy in the structure of the phase that characterizes the liquid crystalline state. While the molecules (mesogens) in the nematic, the simplest of liquid crystal states, are distributed uniformly within the sample (the phase is spatially homogeneous as for the isotropic liquid), they tend to align along a preferred direction (the director) so that the phase is anisotropic and possesses a degree of orientational order. When the orientation of the nematic director varies in a regular helical way along one axis of the sample (characterized by the pitch of the helix), the phase is referred to as a chiral nematic (cholesteric). Phases with additional degrees of positional order are also commonly encountered. The smectic A phase, for example, is a layered structure that possesses a periodic oscillatory molecular density along the nematic director; in this case, the mesogens tend to be preferentially arranged in layers, but there is no long-range positional order within the layer.

The existence of the liquid crystalline state was first recognized by Reinitzer<sup>4</sup> and Lehmann<sup>5</sup> by studying the melting point and optical properties of a cholesterol derivative obtained from carrots; the phase they had discovered was in fact a cholesteric liquid crystal. A wide variety of low molecular

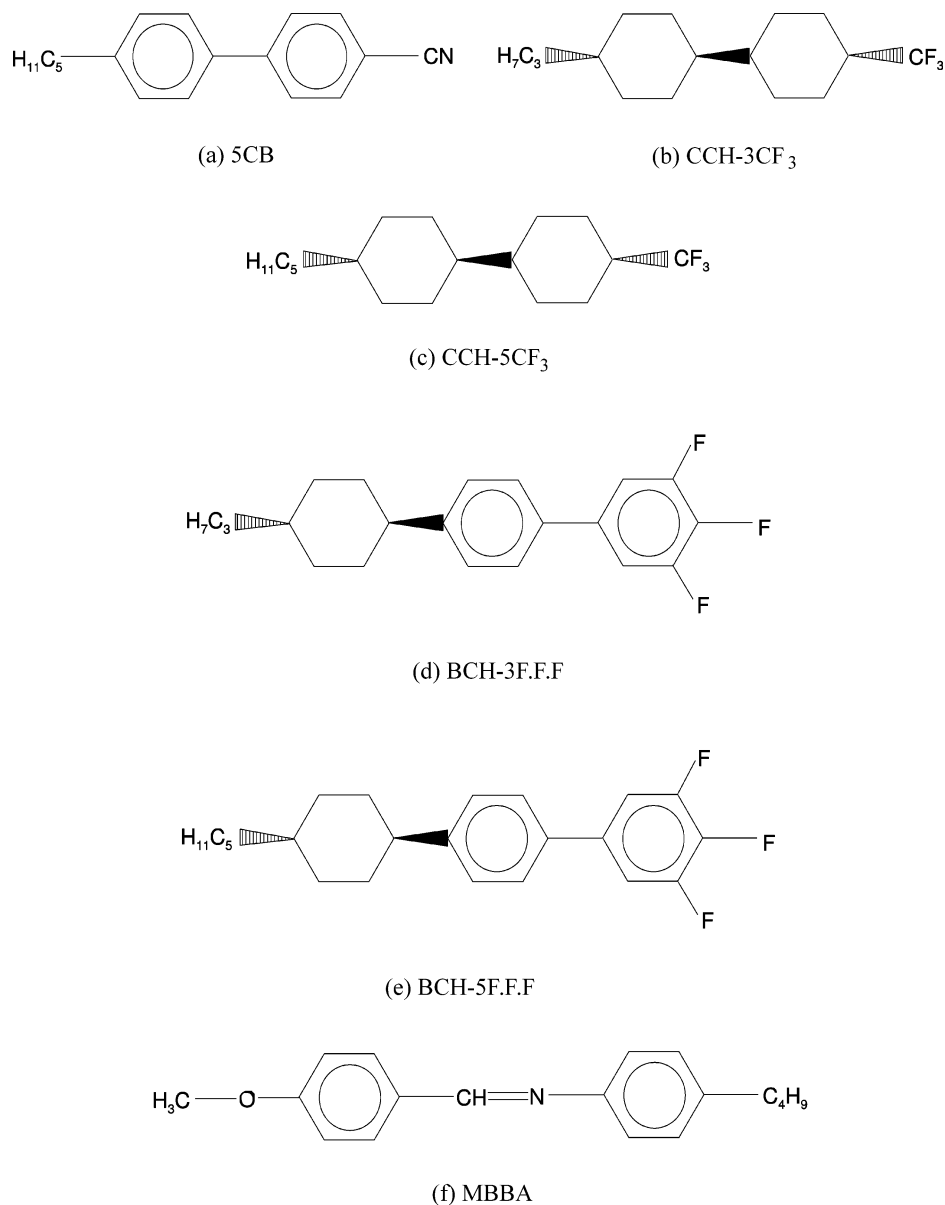
**TABLE 1: Characteristics of the Thermotropic Liquid Crystals Studied**

compound	purity (mass %)	CAS	$T_m$ (K)	$T_{NI}$ (K)
5CB	99.9 <sup>a</sup>	40817-08-1	297.15	308.65
CCH–3CF <sub>3</sub>	99.9 <sup>a</sup>	133261-31-1	313.95	313.85
CCH–5CF <sub>3</sub>	99.9 <sup>a</sup>	140911-33-7	307.15	306.15
BCH–3F.F.F	99.8 <sup>a</sup>	132123-39-8	314.05	305.95
BCH–5F.F.F	99.9 <sup>a</sup>	137019-95-5	302.55	330.15
MBBA	98.8 <sup>b</sup>	26227-73-6	291.15 <sup>c</sup>	318.15 <sup>d</sup>

<sup>a</sup> Determined by GC. <sup>b</sup> Determined by GC and HPLC. <sup>c</sup> Reference 39. <sup>d</sup> Reference 40.

weight organic compounds have now been found to exhibit liquid crystalline phases.<sup>1,6–8</sup> One tends to refer to these compounds as thermotropics because of the leading role that temperature plays as a variable in the transitions between the various states. The unique thermodynamic, structural, rheological, and optical properties of liquid-crystalline materials make them suitable for a wide range of optoelectronic applications (e.g., liquid crystal displays (LCDs) in mobile phones, laptop computers, and televisions), and in numerous cosmetic and pharmaceutical formulations.<sup>3</sup> The use of liquid crystals for dynamic scattering displays started to be considered in the early 1960s by RCA, although this was hampered by the unavailability of a material that was nematic at ambient conditions. The synthesis of *n*-(4-methoxybenzylidene)-4-butaniline (MBBA) is particularly important because it was the first time a compound was shown to exhibit a room-temperature nematic phase;<sup>9</sup> the isotropic–nematic transition of MBBA is, however, strongly affected by impurities (owing to its propensity to hydrolyze with increasing temperature), and the compound exhibits a relatively slow response time to an applied electrical field. It was therefore a major breakthrough when Gray et al.<sup>10</sup> discovered the cyanobiphenyl (CB) room-temperature nematic

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**Figure 1.** Structural formulas of the thermotropic liquid crystals studied.

mesogens that are chemically stable over a large temperature range and are characterized by a large positive dielectric anisotropy and strong birefringence, which makes them ideal materials for use in twisted nematic (TN) cells that had been invented only a few years earlier.<sup>11,12</sup> Although displays with vertically aligned (VA) geometries are becoming increasingly important, the TN cell still remains the workhorse of the industry. The formulations of choice in the development of materials for use in modern optoelectronic devices now tend to be mixtures of fluorinated aromatic compounds of the type that are studied in our paper. The fluorinated materials have improved characteristics, such as an increased nematic temperature range, a larger birefringence and dielectric anisotropy, and a lower viscosity, which allows for lower operating voltages and quicker response times in LCDs.<sup>13–16</sup>

Considering the importance and the large body of existing work on the physical properties of liquid crystalline compounds,<sup>6–8</sup> it is rather surprising that there is a scarcity of vapor pressure data for thermotropics; this is due to the difficulty in measuring the very low volatility of these materials. In the case of some of the liquid crystals studied in this work, the vapor pressures calculated by group contribution methods,<sup>17</sup> which

allow a wide variety of physical properties to be estimated using only information about the functional groups present in the molecule (see references 18–20 for general details of such methods), or reported in the literature at discrete temperatures<sup>21</sup> are found to be much lower than 1 Pa at ambient temperature ( $10^{-4}$  to  $10^{-3}$  Pa). A limited number of experimental studies of the vapor–liquid equilibria of solutions of thermotropic liquid crystals have also been undertaken (see, for example, references 22–26), but, in this case, the vapor pressure of the mixture is dominated by that of the more volatile solvent. There appears to be a large degree of inconsistency in the scarce vapor pressure data that are available for pure thermotropic compounds, bringing their reliability into question. A complete knowledge of fluid phase equilibria is not only of fundamental and practical importance, but invaluable in the development of an accurate molecular description of the thermodynamic properties and phase behavior of liquid crystalline systems, which has been hampered by a lack of basic experimental data, such as vapor pressure and density, for the pure substances.

The main aim of our paper is to provide reliable measurements of the vapor pressure and density of some key thermotropic liquid crystals: MBBA, 4'-cyano-4-*n*-pentylbiphenyl

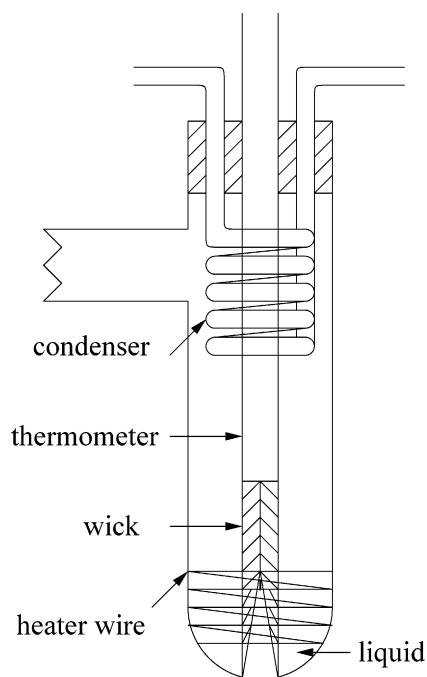


Figure 2. Reflux cell.

(5CB), and a number of industrially relevant trifluorinated bicyclohexyl and cyclohexylbiphenyl derivatives. The effusion,<sup>27–29</sup> gas saturation,<sup>30</sup> and spinning rotor<sup>31–33</sup> methods are commonly used to measure low pressures. However, these approaches require expensive equipment and are limited to a maximum pressure of the order of 1 Pa. In the present work we have constructed an apparatus suitable for measurements of vapor pressures between 0.1 and 1333 Pa in the temperature range 298–523 K, and used it to study the liquid crystalline compounds. In the case of density, only limited experimental data have been reported other than at ambient temperature or close to the various ordering transitions. For example, high-resolution data for the density of 4'-cyano-4-*n*-octylbiphenyl (8CB)<sup>34</sup> and 4'-cyano-4-*n*-octyloxybiphenyl (8OCB)<sup>35</sup> have been measured in the vicinity of the nematic–smectic A transition to allow for a determination of the isobaric thermal expansion and isothermal compressibility coefficients and the corresponding critical exponents that characterize the singularities in these thermodynamic quantities; some data are also available for mixtures of related compounds such as 9CB + 10CB.<sup>36</sup> Apart from 5CB, for which densities at atmospheric pressure as a function of the temperature have been reported,<sup>37,38</sup> data for the

fluid phase of other thermotropic liquid crystals are not available over a significant range of temperature. Accordingly, such measurements were made in the present work for selected thermotropic materials.

## 2. Materials

Six thermotropic liquid crystals with different molecular structures were examined in our work. The characteristics and the chemical formula of these substances are given in Table 1 and Figure 1, respectively. Here,  $T_m$  is the melting temperature, and  $T_{NI}$  is the temperature of the nematic–isotropic phase transition at ambient pressure. Except for MBBA, which was synthesized by SYNTHON Chemicals GmbH and Co. KG, all of the substances were supplied by Merck KGaA. These compounds were used without further purification, and all the data presented in the table were reported by the suppliers or obtained from the literature.

## 3. Vapor Pressures Measurements

**3.1. Experimental Method.** Numerous techniques have been described for the measurement of vapor pressures.<sup>27–33,41,42</sup> The ebulliometric method of Ramsay and Young<sup>43</sup> as implemented by Thomas et al.<sup>44</sup> was chosen for its suitability and its reliability for measurements at pressures below 1 Pa and at high temperatures. In this method, the liquid refluxes under an inert buffer gas in a glass reflux cell (shown schematically in Figure 2), fitted with an electric heater, a condenser, and a thermometer. This reflux cell is connected via a glass tube to a precision manometer and a ballast volume (or a manostat device) to ensure a constant pressure. The utilization of this volume of inert gas allows the pressure transducer to be operated at ambient temperature without condensation phenomenon. During heating, the liquid evaporates rapidly, condenses in the upper part of the cell, and runs back down to the pool at the bottom. An interface between the pure vapor and the inert gas is then established somewhere in the middle of the cell, and the steady-state temperature and pressure are measured. At low pressures, especially as the pressure gradient in the liquid pool becomes significant compared to the equilibrium vapor pressure, superheating is a potentially serious problem. Indeed, at pressures below 100 Pa, the hydrostatic head in the liquid is comparable to, or greater than, the vapor pressure being measured. The modification due to Thomas et al.<sup>44</sup> is the introduction of a wick (made of glass-fiber in the current work) fixed to the end of the thermometer, which sucks up the liquid and establishes intimate contact between the liquid and the vapor around the

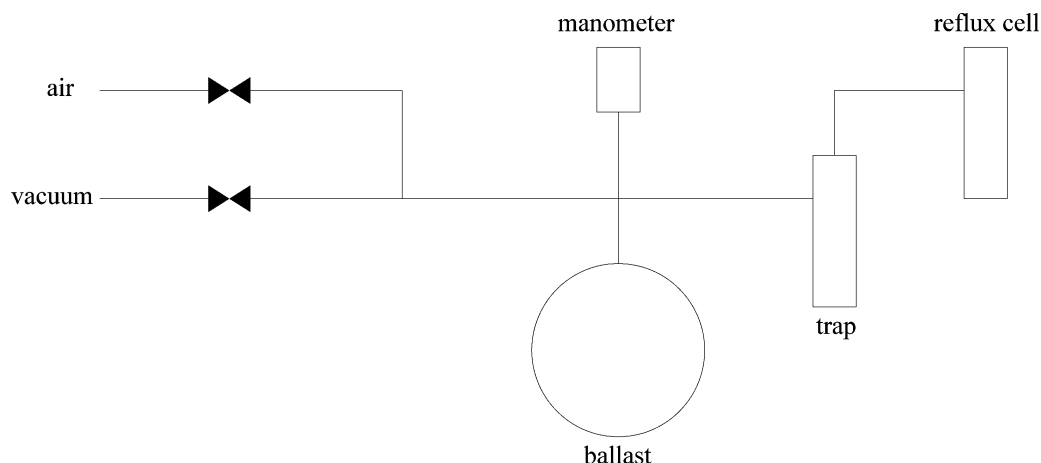
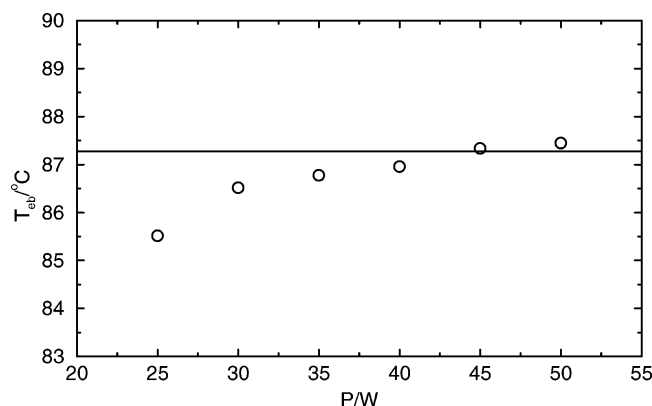
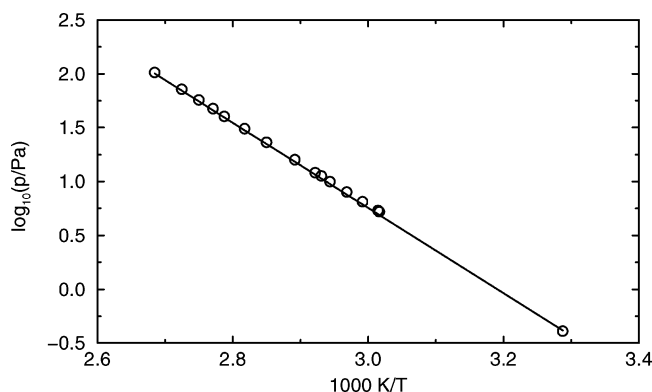


Figure 3. Vacuum line.



**Figure 4.** Ebullition temperatures for *n*-hexadecane as a function of the heater power under a constant pressure of 44.06 Pa. The symbols are the experimental values, and the horizontal line represents the temperature reported in the literature.<sup>45</sup>



**Figure 5.** Vapor pressures of *n*-hexadecane as a function of temperature. Symbols are the experimental measurements, and the line represents the values reported in the literature.<sup>45</sup> The uncertainty of the ebullition temperature corresponds to the width of the symbols.

**TABLE 2: Coefficients *A*, *B*, and *C* for the Calculation of the Vapor Pressure of the Thermotropic Liquid Crystals**

compound	<i>A</i>	<i>B</i>	<i>C</i>	$\Delta_{\text{AAD}}$
5CB	16.849	6870	+30.04	0.036
CCH-3CF <sub>3</sub>	8.053	1104	-183.99	0.019
CCH-5CF <sub>3</sub>	10.136	2359	-99.93	0.031
BCH-3F.F.F	13.598	4950	+12.52	0.045
BCH-5F.F.F	10.631	2834	-109.03	0.028
MBBA	11.893	3496	-90.61	0.033

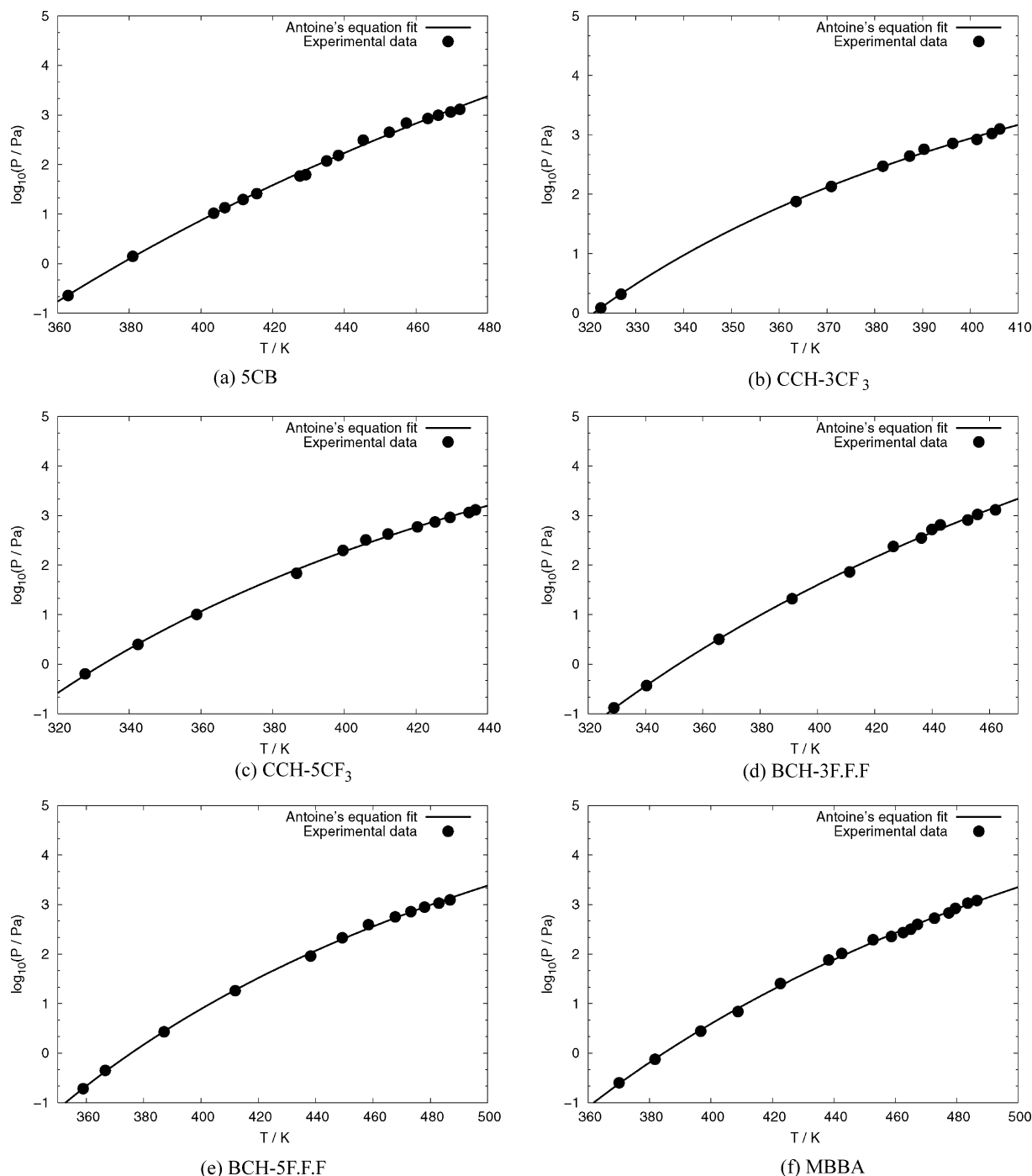
thermometer probe, thereby promoting the establishment of the equilibrium ebullition temperature at the pressure of the buffer gas.

The cell, fabricated from 2 mm thick borosilicate glass, measured 140 mm in height and 36 mm in outside diameter (OD). Temperatures were measured with a stainless-steel-cased platinum resistance thermometer (PRT) probe with an OD of 3 mm and a nominal resistance of 100  $\Omega$  at  $T = 273.15$  K. This probe was calibrated between 273 and 523 K by comparison with a 25  $\Omega$  standard PRT, that had itself been calibrated according to ITS-90<sup>46</sup> between 233 and 523 K at the U.K. National Physical Laboratory. The condenser coil was constructed from a 3.5 mm OD copper tube and was connected to a thermostatically-controlled circulating water bath. For compounds that were solid at ambient temperature, the temperature of the cooling water was set slightly above the melting temperature of the substance under study. The thermometer and the condenser tubes passed through tubular openings in the glass lid of the reflux cell to which they were sealed with an epoxy resin (Stycast 2850 FT). The vapor pressure of the epoxy resin

**TABLE 3: Vapor Pressures of Thermotropic Liquid Crystals as a Function of Temperature and Deviations  $\Delta = \log_{10}(p/\text{Pa}) - \log_{10}(p_{\text{calc}}/\text{Pa})$**

<i>T</i> /K	$\log_{10}(p/\text{Pa})$	$\Delta$	<i>T</i> /K	$\log_{10}(p/\text{Pa})$	$\Delta$
5CB			CCH-3CF <sub>3</sub>		
362.98	-0.638	+0.007	322.66	0.093	+0.004
380.95	0.152	-0.019	326.86	0.322	-0.001
403.49	1.021	-0.019	363.50	1.877	-0.024
406.57	1.130	-0.016	370.93	2.133	-0.013
411.73	1.293	-0.007	381.65	2.471	+0.005
415.50	1.419	-0.010	387.27	2.643	+0.023
427.62	1.765	-0.073	390.35	2.756	+0.055
429.23	1.794	-0.096	396.27	2.859	+0.009
435.14	2.072	-0.008	401.34	2.924	-0.048
438.29	2.184	+0.004	404.45	3.023	-0.021
445.20	2.497	+0.104	406.17	3.095	+0.011
452.49	2.655	+0.044			
457.22	2.834	+0.084			
463.37	2.935	+0.010			
466.23	2.990	-0.016			
469.73	3.066	-0.037			
472.15	3.112	-0.057			
CCH-5CF <sub>3</sub>			BCH-3F.F.F		
327.65	-0.201	+0.021	328.95	-0.886	+0.012
342.45	0.393	-0.017	340.37	-0.432	-0.003
358.82	1.004	-0.021	365.71	0.498	-0.13
386.65	1.839	-0.076	391.16	1.323	-0.012
399.59	2.300	+0.036	411.18	1.860	-0.055
406.01	2.505	+0.076	426.44	2.370	+0.049
412.21	2.628	+0.046	436.28	2.543	-0.026
420.33	2.775	+0.001	440.00	2.722	+0.063
425.23	2.870	-0.017	442.84	2.818	+0.090
429.49	2.963	-0.015	452.46	2.911	-0.042
434.73	3.065	-0.026	455.81	3.025	-0.004
436.66	3.115	-0.016	462.10	3.110	-0.059
BCH-5F.F.F			MBBA		
358.93	-0.721	-0.011	370.09	-0.602	+0.014
366.70	-0.347	+0.021	381.68	-0.119	-0.001
387.03	0.436	0.000	396.66	0.450	-0.020
412.04	1.262	-0.016	408.84	0.843	-0.064
438.24	1.955	-0.067	422.63	1.403	+0.039
449.31	2.329	+0.027	438.26	1.881	+0.044
458.49	2.591	+0.070	442.49	2.014	+0.056
467.70	2.751	+0.022	452.83	2.293	+0.052
473.10	2.855	+0.009	458.73	2.360	-0.036
477.97	2.954	+0.005	462.66	2.440	-0.052
483.03	3.028	-0.025	465.00	2.505	-0.050
486.82	3.096	-0.093	467.33	2.600	-0.013
			472.66	2.724	-0.018
			477.41	2.830	-0.025
			479.60	2.919	+0.013
			483.67	3.034	+0.035
			486.58	3.084	+0.024

is unknown, possibly ill-defined, and almost certainly negligible; we did not observe any significant outgassing into the empty cell. The thermometer extended to about 1 cm above the liquid surface, and the coil was arranged so that cold condensate dripped directly into the liquid pool without striking the thermometer (see Figure 2). The connection between the lid and the cell was made with a demountable B34 ground-glass joint sealed with a thin film of vacuum grease (Apiezon type M, vapor pressure  $< 10^{-8}$  Pa). The heater consisted of a length of nickel-chrome wire with a resistance of about 50  $\Omega$  wrapped around the lower 20 mm of the cell and connected via PTFE-insulated copper extension leads to a variable (0–50 W) power supply. The joints in the wire were made with a high-melting-point soft solder, and the heater was held down by polyimide adhesive tape permitting operation up to about 573 K. As shown schematically in Figure 3, the cell was connected via a 22 mm OD (wall thickness 2 mm) glass tube, through a liquid-nitrogen-cooled trap, to a ballast volume of about 4 L. The pressure was



**Figure 6.** Vapor pressures of the thermotropic liquid crystals as a function of temperature. The uncertainty of the ebullition temperature, not represented in the figure, corresponds to the width of the symbols.

measured with an accuracy of  $\pm 0.15\%$  of reading and a resolution of  $\pm 10$  mPa with a 0–1333 Pa capacitance manometer (BOC–Edwards Barocel model 622) connected to the ballast volume. A first valve permitted the system to be evacuated to a pressure below 10 mPa, and a second (micrometering) valve permitted buffer gas to be admitted into the system when desired to increase the pressure. The vacuum system comprised a primary oil-sealed rotary pump and a secondary air-cooled oil–vapor diffusion pump capable of an ultimate vacuum of better than 0.1 mPa.

**3.2. Testing of the Apparatus.** The performance of the apparatus was tested by means of measurements on normal hexadecane ( $n\text{-C}_{16}\text{H}_{34}$ ) (Sigma-Aldrich, purity 99 mass%). This system was chosen because reliable vapor pressure data are

**TABLE 4: Densities of the Thermotropic Liquid Crystals as a Function of Temperature in the Nematic Phase and Absolute Deviations  $\Delta = \rho - \rho_{\text{calc}}$**

$T/\text{K}$	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\Delta/\text{kg}\cdot\text{m}^{-3}$	$T/\text{K}$	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\Delta/\text{kg}\cdot\text{m}^{-3}$
5CB			BCH-5F.F.F		
292.99	1024.89	−0.05	308.59	1098.37	−0.11
298.86	1019.63	+0.11	318.08	1090.30	+0.17
303.21	1015.44	−0.06	322.66	1086.24	+0.13
			327.24	1081.89	−0.19
MBBA					
292.62	1044.77	−0.27			
303.45	1039.10	+0.13			
308.44	1035.05	+0.30			
313.17	1031.00	+0.24			
317.85	1026.40	−0.40			



**TABLE 5: Densities of the Thermotropic Liquid Crystals as a Function of Temperature in the Isotropic Phase and Absolute Deviations  $\Delta = \rho - \rho_{\text{calc}}$** 

<i>T</i> /K	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\Delta/\text{kg}\cdot\text{m}^{-3}$	<i>T</i> /K	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\Delta/\text{kg}\cdot\text{m}^{-3}$
5CB			CCH-3CF <sub>3</sub>		
308.42	1006.96	+0.34	322.64	998.44	+0.03
313.12	1002.93	−0.04	332.18	990.60	−0.01
327.91	991.02	−0.47	341.48	982.97	−0.05
338.16	983.32	−0.22	351.50	974.84	+0.01
346.54	977.11	+0.08	360.58	967.43	+0.02
354.48	971.29	+0.42			
367.78	960.43	−0.11			
CCH-5CF <sub>3</sub>			BCH-3F.F.F		
313.45	989.28	+0.14	308.52	1121.67	+0.11
322.57	981.84	−0.10	311.35	1119.31	+0.04
332.67	973.74	−0.23	313.10	1117.77	−0.09
341.39	967.26	+0.17	318.13	1113.75	−0.04
350.25	960.15	+0.05	322.78	1110.00	−0.03
361.06	951.54	+0.03	332.56	1102.07	−0.03
			341.85	1094.61	0.00
			350.10	1088.00	+0.06
BCH-5F.F.F			MBBA		
332.39	1075.81	+0.09	322.63	1020.84	+0.06
341.96	1068.00	−0.13	332.58	1013.15	−0.05
351.92	1060.30	−0.01	341.83	1006.13	−0.02
360.06	1053.53	+0.05	350.13	999.76	−0.07
			361.20	991.46	+0.07

available in the temperature and pressure ranges considered in this work.<sup>45</sup> The buffer gas was chosen as air for convenience and because the solubilities of oxygen and nitrogen, which are, in terms of mole fraction at atmospheric pressure, of the order of  $10^{-3}$  in alkanes<sup>47,48</sup> and  $10^{-4}$  in liquid crystals,<sup>49</sup> which was judged to be insignificant at pressures below 1333 Pa.

A quantity of about 15 mL of *n*-hexadecane was placed in the cell, and the liquid was degassed for 12 h under the action of the primary pump and for 2 additional hours with the secondary pump. The pressure was then set to the desired value by introducing air through the micrometering valve. The heater was then switched on to warm the liquid, and, after a few minutes, boiling was observed. Under a constant pressure of 44.06 Pa, the temperature recorded by the thermometer was constant to within 1 K for heater powers between 30 and 50 W, as illustrated in Figure 4. The difference between the mean ebullition temperature under a constant pressure of 44.06 Pa and the ebullition temperature reported in reference 45 was about −0.60 K. The system was sufficiently leak tight to permit operation at constant pressure with the vacuum valve completely shut. This helped to ensure that the indicated pressure was a true measure of the pressure in the reflux cell. The experimental evaporation temperatures of hexadecane obtained are compared with values from the literature<sup>45</sup> in Figure 5. It is clear from this figure that the agreement with the literature values<sup>45</sup> is satisfactory, with the present results systematically about 0.6 K below the literature data across the pressure range investigated; the precision of the literature data is about  $\pm 0.15$  K.

#### 4. Density Measurements

The densities of the liquid crystals were measured at ambient pressure and at temperatures between 293 and 368 K with a borosilicate glass pycnometer. The pycnometer consisted of a 35 cm<sup>3</sup> reservoir fitted with a 2.2 mm internal diameter (ID) capillary of length 290 mm. The volume was calibrated as a function of the height of the liquid in the capillary with distilled water. The mass of the pycnometer empty and when filled with liquid was determined with an electronic mass comparator

(Mettler Toledo model PR 5003) with a precision of  $\pm 1$  mg. The height of the liquid in the capillary was measured with a digital cathetometer with a precision of  $\pm 0.01$  mm. The pycnometer was placed in a water bath where the temperature was maintained constant to within  $\pm 0.02$  K. The temperature was measured with a resolution of  $\pm 0.01$  K with a 100  $\Omega$  PRT probe model, which was calibrated between 273 and 523 K in the same way as the PRT used for the vapor pressure measurements. The pycnometer was filled using a glass syringe fitted with a 300 mm-long needle. Compounds that were solid at ambient temperature were first heated above their melting point; the pycnometer, syringe, and needle were also warmed to prevent solidification of the sample.

#### 5. Results and Discussion

**5.1. Vapor Pressure of Liquid Crystals.** The vapor pressure of each liquid crystal listed in Table 1 was measured as a function of the temperature, and the results have been correlated by means of Antoine's equation:

$$\log_{10}(p/\text{Pa}) = A - \frac{B}{(T/\text{K}) + C} \quad (1)$$

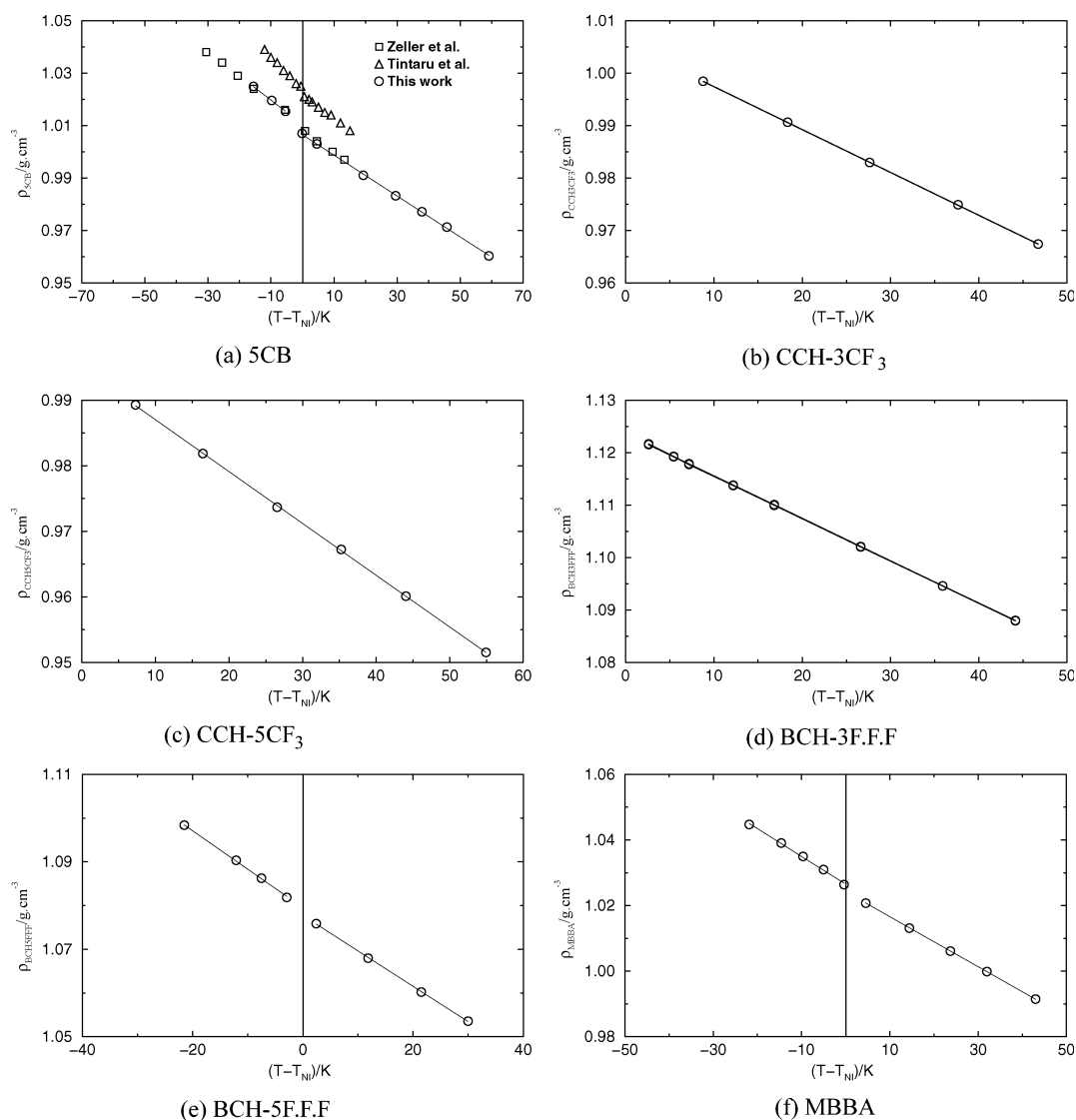
Here, *A*, *B*, and *C* are the coefficients of the equation, and *T* is the temperature. The values of the coefficients *A*, *B*, and *C* and the absolute average deviation (AAD) of  $\log_{10}(p/\text{Pa})$  from Antoine's equation are listed in Table 2. This AAD provides an estimate of the precision of the results.

The measured vapor pressures and the deviations from Antoine's equation are listed in Table 3 and are also illustrated in Figure 6.

Very limited experimental data for the vapor pressures of liquid crystals are reported in the literature. It is possible, nevertheless, to compare our measurements with data from other sources at some temperatures in the case of the 5CB, CCH-3CF<sub>3</sub>, CCH-5CF<sub>3</sub>, and MBBA. A vapor pressure of 66.50 Pa at 423 K is reported by Sigma-Aldrich<sup>21</sup> for 5CB of 98% purity. This value is 25% higher than the one measured in our current study. For this same compound, Yasuyuki<sup>50</sup> give an upper bound for the vapor pressure of 1 Pa at 373 K, which is in agreement with the value of 0.65 Pa measured in our work. For the same compound, one can use group contribution methods to estimate a vapor pressure of 3 mPa at 298 K,<sup>17</sup> whereas extrapolation of our correlation (eq 1) for 5CB gives the much smaller value of 0.1 mPa. Finally, Gonzalo et al.<sup>51</sup> have reported the normal boiling temperature as being higher than 673 K, while we estimate a value of 550 K from the Antoine equation (eq 1).

In the case of the fluorinated thermotropics CCH-3CF<sub>3</sub> and CCH-5CF<sub>3</sub>, normal boiling temperatures of 583 and 609 K, respectively, are stated in the Merck product specification, whereas an extrapolation of eq 1 yields 546 and 560 K, respectively.

For MBBA, Krestov et al.<sup>52</sup> report vapor pressures of between 30 and 230 Pa in the temperature range 288–323 K. However, the pressures that we measured for this compound are very low ( $\sim 0.25$  Pa at 363 K), and it was impossible to make measurements at temperatures as low as 323 K because the lowest pressure measurable with our approach was about 0.1 Pa. The vapor pressure calculated at 323 K from eq 1 for MBBA is 1 mPa, which is about  $10^5$  times lower than that reported by Krestov et al. The vapor pressure of MBBA measured by Molga et al.<sup>23</sup> using a static method<sup>42</sup> is  $< 2$  Pa at 303 K. Finally, a vapor pressure of 0.3 mPa at 298 K can be estimated with group contribution methods.<sup>17</sup>



**Figure 7.** Densities of thermotropic liquid crystals expressed as a function of the difference between the experimental temperature and the temperature of the nematic–isotropic phase transition ( $T_{NI}$ ). The symbols are the experimental data, and the lines correspond to eq 2.

**5.2. Density of Liquid Crystals.** The densities of the liquid crystals described in section 2 were measured as a function of the temperature in the nematic and isotropic phases with a precision of  $\pm 0.003\%$ . This precision was calculated according to the Skoog rules<sup>53</sup> by propagation of the uncertainty of the mass and the volume of liquid in the pycnometer. In each phase, the densities have been expressed as a function of temperature by a linear correlation:

$$\rho(T)/\text{kg}\cdot\text{m}^{-3} = a_0 + a_1[(T - T_{NI})/\text{K}] \quad (2)$$

Here,  $a_0$  and  $a_1$  are parameters,  $T$  is the actual temperature, and  $T_{NI}$  is the temperature of the nematic–isotropic phase transition (clearing point), as given in Table 1.

The measured densities and the absolute deviations from the correlation are listed for the nematic and isotropic phases in Tables 4 and 5, respectively. These experimental data are also illustrated in Figure 7.

The values of the coefficients  $a_0$ ,  $a_1$  and the AAD of the correlation are listed for the nematic and isotropic phases in Tables 6 and 7, respectively.

In the case of 5CB, the measured densities are compared with values from the literature in Figure 7a. The data given by Zeller

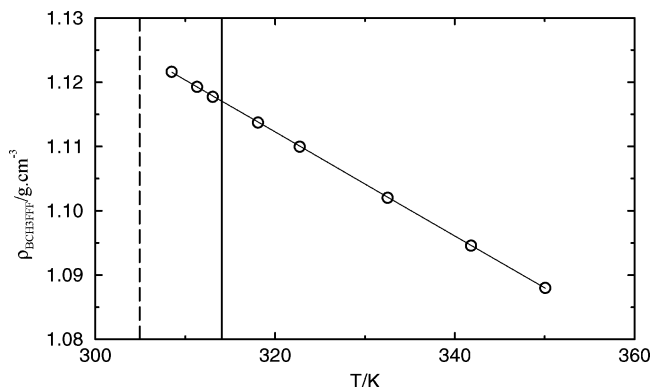
**TABLE 6: Coefficients  $a_0$  and  $a_1$  for the Correlation of the Densities in the Nematic Phase**

compound	$a_0$	$a_1$	$\Delta_{AAD}/\text{kg}\cdot\text{m}^{-3}$
5CB	1010.48	−0.9230	0.07
BCH-5F.F.F	1079.52	−0.8798	0.16
MBBA	1026.55	−0.8451	0.27

**TABLE 7: Coefficients  $a_0$  and  $a_1$  for the Correlation of the Densities in the Isotropic Phase**

compound	$a_0$	$a_1$	$\Delta_{AAD}/\text{kg}\cdot\text{m}^{-3}$
5CB	1006.44	−0.7762	0.24
CCH-3CF <sub>3</sub>	1005.59	−0.8170	0.02
CCH-5CF <sub>3</sub>	994.90	−0.7892	0.12
BCH-3F.F.F	1123.64	−0.8085	0.05
BCH-5F.F.F	1077.70	−0.8097	0.07
MBBA	1024.19	−0.7619	0.05

et al.<sup>38</sup> are in close agreement with our results (AAD of 0.08%), although these authors give neither the uncertainty of their measurements nor the purity of their sample. The value of  $1002.4 \text{ kg}\cdot\text{m}^{-3}$  reported at 314 K by Sen et al.<sup>54</sup> is also consistent with our measurements. Tintaru et al.<sup>37</sup> measured the density of a 98% pure sample of 5CB by capillarimetry with a claimed uncertainty of  $\pm 0.3\%$ ; however, their results differ



**Figure 8.** Densities of the fluorinated thermotropic mesogen BCH-3F.F.F as a function of temperature. The vertical line represent the melting temperature, and the dashed line represents the temperature of nematic-isotropic phase transition ( $T_{NI}$ ).

from ours by about 1.5%. For MBBA, de Jeu et al.<sup>55</sup> quote a value of  $1050 \text{ kg}\cdot\text{m}^{-3}$  at 292 K, which is in line with our experimental values. Among the compounds studied, it is interesting to note that CCH-3CF<sub>3</sub>, CCH-5CF<sub>3</sub>, and BCH-3F.F.F all have nematic-isotropic phase transition temperatures that are lower than the equilibrium melting temperature (see Table 1). For example, in the case of BCH-3F.F.F,  $T_{NI}$  is 8.1 K lower than the melting temperature; such a system is referred to as monotropic. When the solid is warmed, one observes the transition from solid to isotropic liquid at the equilibrium melting temperature. However, upon cooling, a metastable isotropic liquid persists below the melting temperature, and one can observe the transition to the nematic phase at  $T_{NI}$ . The densities of this metastable liquid, measured during cooling, are included in Table 5 and shown in Figure 8. One can see from the figure that  $\rho(T)$  is continuous in both value and slope at the equilibrium melting temperature. The AAD of the correlation is of 0.005% in the temperature range considered.

In the cases of CCH-3CF<sub>3</sub> and CCH-5CF<sub>3</sub>,  $T_{NI}$  is only 0.1 and 1.0 K, respectively, below the melting temperature, and no density measurements were made in these small intervals.

## 6. Conclusions

An apparatus has been constructed that is suitable for measurements of vapor pressures between 0.1 and 1333 Pa in the temperature range 298–523 K. The apparatus has been validated by means of measurements on *n*-hexadecane, and new results are reported for six thermotropic liquid-crystalline materials. This represents one of the first reliable measurements of the saturation pressure of such systems over a moderately wide temperature range. The densities of these same substances have been measured at atmospheric pressure at temperatures between 293 and 368 K by a pycnometric method. In future work we plan to use this vapor-liquid equilibria data to develop and refine accurate molecular parameters for use in predictive theories of the isotropic and nematic states of such systems.

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## References and Notes

- (1) Chandrasekhar, S. *Liquid Crystals*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1992.
- (2) de Gennes, P.-G.; Prost, J. *The Physics of Liquid Crystals*, 2nd ed.; Oxford University Press: Oxford, 1993.

- (3) Collins, P. J. *Liquid Crystals. Nature's Delicate Phase of Matter*, 2nd ed.; Princeton University Press: Princeton, NJ, 2002.
- (4) Reinitzer, F. *Monatsh. Chem.* **1888**, 9, 421.
- (5) Lehmann, O. Z. *Phys. Chem. (Leipzig)* **1889**, 4, 462.
- (6) Vill, V. *LiqCryst 4.7: Database of Liquid Crystalline Compounds*; LCI Publishers GMBH, Hamburg, 2008; <http://liqcryst.chemie.uni-hamburg.de>
- (7) Demus, D.; Goodby, J. W.; Gray, G. W.; Spiess, H.-W.; Vill, V. *Handbook of Liquid Crystals*; Wiley-VCH: Weinheim, 1998.
- (8) Dumnur, D. A.; Fukuda, A.; Luckhurst, G. R., Eds. *Physical Properties of Liquid Crystals: Nematics*; EMIS Datareviews Series No. 25; INSPEC: London, 2001.
- (9) Kelker, H.; Scheurle, B. *Angew. Chem.* **1969**, 81, 903.
- (10) Gray, G. W.; Harrison, K. J.; Nash, J. A. *Electron. Lett.* **1973**, 9, 130.
- (11) Leslie, F. M. *Mol. Cryst. Liq. Cryst.* **1970**, 12, 57.
- (12) Schadt, M.; Helfrich, W. *Appl. Phys. Lett.* **1971**, 18, 127.
- (13) Pauluth, D.; Tarumi, K. *J. Mater. Chem.* **2004**, 14, 1219.
- (14) Pauluth, D.; Tarumi, K. *J. Soc. Info. Displays* **2005**, 13, 693.
- (15) Takatsu, H.; Takehara, S.; Takeuchi, K.; Iwashita, Y. *Proc. SPIE* **2001**, 4463, 92.
- (16) Hird, M. *Chem. Soc. Rev.* **2007**, 36, 2070.
- (17) *Advanced Chemistry Development (ACD/Labs) Software V8.14 for Solaris*; ACD Labs: Toronto, 1994–2007.
- (18) Joback, K. G.; Reid, R. C. *Chem. Eng. Commun.* **1987**, 57, 233.
- (19) Constantinou, L.; Gani, R.; O'Connell, J. P. *Fluid Phase Equilib.* **1995**, 103, 11.
- (20) Lymperiadis, A.; Adjiman, C. S.; Galindo, A.; Jackson, G. J. *Chem. Phys.* **2007**, 127, 234903.
- (21) *Sigma-Aldrich Product Detail 5CB*; Sigma-Aldrich: St. Louis, MO, 2006.
- (22) Woycicki, W.; Stecki, J. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1974**, 22, 241.
- (23) Molga, E.; Stecki, J. *J. Chem. Thermodyn.* **1977**, 9, 79.
- (24) Jackowski, A. W. *J. Chem. Thermodyn.* **1985**, 17, 865.
- (25) Jackowski, A. W. *J. Chem. Thermodyn.* **1988**, 20, 721.
- (26) Jackowski, A. W. *J. Chem. Thermodyn.* **1992**, 24, 601.
- (27) *NF T 20-047 AFNOR: Chemical Products for Industrial Use. Determination of vapour pressure of solids and liquids within range from  $10^{-3}$  to 1 Pa. Vapour pressure balance method*, 1985.
- (28) Knudsen M. *Ann. Phys. (Leipzig)* **1909**, 29, 1979; **1911**, 34, 593.
- (29) Gückel, W.; Synnatschke, G.; Rittig, F. R. *Pestic. Sci.* **1973**, 4, 137.
- (30) *CFR Part 796*; Office of the Federal Register: Washington, D.C., 1993; p 148.
- (31) Messer, G.; Röhl, P.; Grosse, G.; Jitschin, W. *J. Vac. Sci. Technol.* **1987**, 5 (4), 2440.
- (32) Comsa, G.; Fremerey, J. K.; Lindenau, B.; Röhl, P. *J. Vac. Sci. Technol.* **1980**, 17 (2), 642.
- (33) Fremerey, J. K. *J. Vac. Sci. Technol.* **1985**, 3 (3), 1715.
- (34) Żywociński, A.; Wieczorek, S. A.; Stecki, J. *Phys. Rev. A* **1987**, 36, 1901.
- (35) Żywociński, A.; Wieczorek, S. A. *J. Phys. Chem. B* **1997**, 101, 6970.
- (36) Raja, V. N.; Prasad, S. K.; Rao, D. S. S.; Chandrasekhar, S. *Liq. Cryst.* **1992**, 12, 239.
- (37) Tintaru, M.; Moldovan, R.; Belca, T.; Frunza, S. *Liq. Cryst.* **2001**, 28, 793.
- (38) Zeller, H. R. *Phys. Rev. A* **1982**, 26, 1785.
- (39) Stephens, C. E.; Sinnadurai, F. N. *J. Phys. E: Sci. Instrum.* **1974**, 7, 641.
- (40) Dunmur, A.; Fukuda, A.; Luckhurst, R. *Physical Properties of Liquid Crystals: Nematics*; EMIS Data Reviews Series No. 25; INSPEC: London, 2001; p 134.
- (41) Glasstone, S. *Textbook of Physical Chemistry*, 2nd ed.; Van Nostrand Company: New York, 1946.
- (42) *NF T 20-048 AFNOR: Chemical Products for Industrial Use. Determination of vapour pressure of solids and liquids within range from  $10^{-3}$  to  $10^5$  Pa. Static method*, 1985.
- (43) Ramsay, W.; Young, S. *J. Chem. Soc.* **1885**, 47, 42.
- (44) Thomas, L. H.; Smith, H.; Meatyrd, R. J. *Phys. E: Sci. Instrum.* **1968**, 1, 1119.
- (45) Ambrose, D.; Walton, J. *Pure Appl. Chem.* **1989**, 61, 1395.
- (46) Preston-Thomas, H. *Metrologia* **1990**, 27, 3.
- (47) Riess, J. G. *Chem. Rev.* **2001**, 101, 2797.
- (48) Costa Gomes, M. F.; Deschamps, J.; Padua, A. A. H. *Fluid Phase Equilib.* **2006**, 251, 128.
- (49) Araya, K.; Iwasaki, K. *Mol. Cryst. Liq. Cryst.* **2002**, 392, 49.
- (50) Yasuyuki, T. Liquid crystal display device. *Jpn. Kokai Tokkyo Koho* **1986**, JP 61029819, A2 19860210.



- (51) Gonzalo, J.; Dyer, P. E.; Hird, M. *Appl. Phys. Lett.* **1997**, 71, 2752.  
(52) Krestov, A.; Azarova, G. *Mol. Cryst. Liq. Cryst.* **1990**, 192, 53.  
(53) Skoog, D. A.; West, D. M.; Holler, F. J. *Chimie Analytique*; De Boeck: Paris, 1997.  
(54) Sen, S.; Brahma, P.; Roy, S. K.; Mukherjee, D. K.; Roy, S. B. *Mol. Cryst. Liq. Cryst.* **1983**, 100, 327.  
(55) de Jeu, W. H.; Claassen, W. A. P.; Spruijt, A. M. J. *Mol. Cryst. Liq. Cryst.* **1976**, 37, 269.