

# Density and Speed of Sound Measurements of Methyl- and Propylcyclohexane<sup>†</sup>

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The density and speed of sound of liquid methylcyclohexane and propylcyclohexane were measured with two vibrating-tube densimeters and a time-of-flight method, respectively. The combined range of the data is from 270 to 470 K with pressures to 40 MPa. The estimated uncertainties of the density and the speed of sound data are each 0.1%. The experimental data are represented by correlations within their estimated uncertainty. Comparisons with literature data show good agreement in overlapping ranges. Data presented here constitute a substantial addition to the previously available data for these two compounds.

## 1. Introduction

Cyclic hydrocarbons are of interest as components of fuels and propellants and as reactants in organic syntheses. Engineering design of combustion machinery requires accurate thermo-physical property information over wide temperature and pressure ranges, in particular density and speed of sound. Two different vibrating-tube densimeters and a time-of-flight method were used in this study to measure these properties in the combined range from 270 to 470 K with pressures to 40 MPa. The chemical characterization of the test compounds as well as experimental methods and procedures are described in the next section of this report. The results section outlines how the densities at ambient pressure were obtained from both densimeters and presents the measured speed of sound data at ambient pressure, derived adiabatic compressibilities at ambient pressure, and the measured densities of the compressed liquids. During the measurements, experimental results were periodically correlated with Rackett and Tait equations to monitor repeatability and consistency. In order to facilitate engineering calculations, final versions of these correlations are presented following the results section. The correlations also provide baselines for comparisons of the present results with literature data. These are documented at the end of the paper.

## 2. Test Compounds

Samples of methylcyclohexane (C<sub>7</sub>H<sub>14</sub>, Chemical Abstracts Service Registry Number 108-87-2) and propylcyclohexane (C<sub>9</sub>H<sub>18</sub>, Chemical Abstracts Service Registry Number 1678-92-8) were obtained from a commercial source with specified purities of 99%. They were analyzed with gas chromatography/mass spectrometry (30 m capillary column of 5% phenyl polydimethyl siloxane having a thickness of 1  $\mu$ m, temperature program from 60 to 250 °C, 10 °C·min<sup>-1</sup>). The actual mole fraction of methylcyclohexane was found to be 97.42% with

twelve compounds as impurities, most of them isomeric dimethylcyclohexanes. The actual mole fraction of propylcyclohexane was found to be 96.68% with 2.12%  $\alpha$ -ethylcyclohexanemethanol being the major impurity. Other impurities were 0.51% methylcyclohexane, 0.41% cis-octahydro-1*H*-indene, and 0.28% 1-ethylpropylcyclohexane.

The equilibrium geometries of the test compounds were elucidated by ab initio calculations in the Hartree–Fock approximation with 6-31 G\* basis sets.<sup>1</sup> They are shown in Figure 1 in terms of isoelectron density distribution surfaces at 0.002 and 0.08 electrons·au<sup>-3</sup>, respectively, with the electrostatic potential mapped onto each.<sup>2</sup> The isosurface of electron density 0.002 electrons·au<sup>-3</sup> (with 1 atomic unit = 5.292 nm being the Bohr radius of hydrogen) contains approximately 98% of a molecule. It is rendered as a mesh to indicate the electron cloud. The isosurface of electron density 0.08 electrons·au<sup>-3</sup> is rendered as a solid surface to illustrate the core of the molecule. Such visualizations of molecular, size, shape, and charge distribution facilitate the interpretation of measurement results of macroscopic properties and deepen the understanding of their molecular origins.

## 3. Experimental Details

Two instruments were employed to measure the properties of the test liquids at ambient pressure and at elevated pressures up to 40 MPa. A density and sound speed analyzer DSA 5000 from Anton Paar (In order to describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturers' names or labels. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.) was used to determine these properties at ambient pressure. Temperature scans were programmed from 70 to 10 °C in decrements of 10 °C followed by a single measurement at 5 °C.

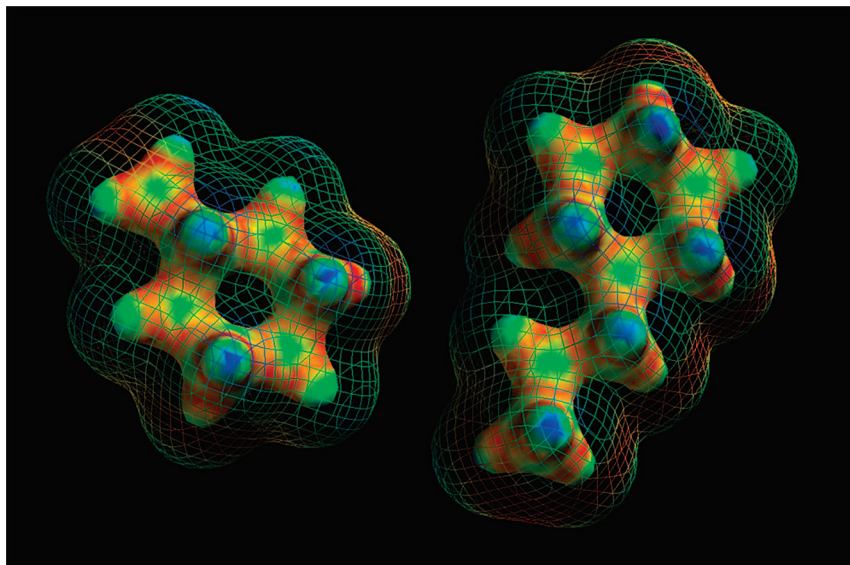
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(1) Hehre, W. J. *A Guide to Molecular Mechanics and Quantum Chemical Calculations*; Wavefunction, Inc.: Irvine, CA, 2003.

(2) Gillespie, R. J.; Popelier, P. L. A. *Chemical Bonding and Molecular Geometry: From Lewis to Electron Densities*; Oxford University Press: New York, 2001.



**Figure 1.** Structure of methyl- and propylcyclohexane in terms of isoelectron density surfaces. The outer and the inner surface represent electron densities of 0.02 and 0.8 electrons $\cdot\text{au}^{-3}$ , respectively.

The device contains a sound speed cell and a vibrating quartz tube densimeter in series. Temperature is measured with an integrated Pt-100 thermometer with an estimated uncertainty of 0.01 K. The sound speed cell has a circular cylindrical cavity of 8 mm diameter and 5 mm thickness that is sandwiched between the transmitter and receiver. The speed of sound is determined by measuring the time-of-flight of signals between the transmitter and receiver.<sup>3</sup> The instrument was calibrated with air and deionized water at 20 °C. The reproducibility of the sound speed of water at 20 °C was ensured to be within 0.01% before and after measurements of the test liquids. Careful cleaning of the sound speed cell with suitable solvents was found critical to avoid contamination and to ensure this level of performance. For the same reason, fresh samples of test liquids were injected for each temperature scan instead of performing repetitive measurements on the same sample. At least four temperature scans were performed for each test liquid. The relative standard deviation of these repeated sound speed measurements was lower than 0.013%. The uncertainty of sound speed measurements with this instrument is quoted by the manufacturer as 0.1%.

The uncertainty of a vibrating quartz tube densimeter, such as that in the DSA 5000, has been assessed by Fitzgerald<sup>4</sup> concluding that it is lower than 0.03 kg $\cdot\text{m}^{-3}$ . The performance of the instrument used in this study was examined with NIST Standard Reference Material 211d “Toluene Liquid Density.” The certified density values of this material at 15, 20, and 25 °C were reproduced by the instrument with deviations between  $-0.011$  and  $-0.026$  kg $\cdot\text{m}^{-3}$ . The uncertainty of the reference values is reported as 0.025 kg $\cdot\text{m}^{-3}$ . Densities of the test liquids were measured in accordance with ASTM D4052 Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter<sup>5</sup> during the same temperature scans that were carried out to obtain their speeds of sound. The instrument corrects the measured densities for the viscosity of the test liquid. The relative standard deviation of repeated density measurements was lower than 0.003%.

Densities of the compressed test liquids were measured with the automated densimeter of Outcalt and McLinden, details of which have been described in a previous publication.<sup>6</sup> Central to the

apparatus is a commercial vibrating-tube densimeter DMA-HPM from Anton Paar Corp. Several physical and procedural improvements have been implemented beyond that of the commercial instrument operated in a stand-alone mode in order to minimize the uncertainty in the measurements. The temperature range of the instrument is 270–470 K, with pressures up to 50 MPa. The estimated uncertainty of the temperature measurement is 30 mK, that of the pressure measurement is at the most 7 kPa. The overall uncertainty in density is 0.64–0.81 kg $\cdot\text{m}^{-3}$ , corresponding to a relative uncertainty range from 0.07% to 0.14%. Once filled with the test liquid, the fully automated instrument measures the densities at preprogrammed pressures and temperatures.

#### 4. Results

The results of the measurements are presented numerically in Tables 1–3 and graphically in Figures 2–5. Adiabatic compressibilities at ambient pressure were obtained from the measured densities and speeds of sound via the thermodynamic relation  $\kappa_s = -(\partial V/\partial p)_s/V = 1/(\rho w^2)$ , where  $V$  denotes volume,  $p$  is pressure,  $\rho$  is the density, and  $w$  is the speed of sound. The subscript  $s$  indicates “at constant entropy  $s$ .” For convenience, the calculated adiabatic compressibilities are included in Table 1.

The speed of sound and adiabatic compressibility data of the two test liquids at ambient pressure are plotted in Figures 2 and 3 as a function of temperature. Comparing the plots illustrates how changing the molecular structure of methylcyclohexane by adding an ethyl-group ( $-\text{CH}_2-\text{CH}_2-$ ) to the aliphatic side chain to form propylcyclohexane influences the macroscopic properties of the two compounds. The speed of sound increases between 5.1% at 273.15 K and 8.1% at 343.15 K whereas the adiabatic compressibility increases between 13.8% and 21.4%. The densities of the test liquids at these two state points differ by only 3% and 4%, respectively. Thus, the adiabatic compressibility appears to reflect structural changes on the molecular scale with higher resolution than the other two properties.

The results of the density measurements at ambient pressure are included in Table 1 and those of the wide-ranging measurements are listed in Tables 2 and 3. Graphical representations of the density data from both instruments are shown in Figures 4 and 5 for each test liquid. The measurements at elevated pressures were spaced below 5 MPa in

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(4) Fitzgerald, D. Technical Assessment of Anton Paar DMA5000. H&D Fitzgerald, 2000, <http://www.density.co.uk>.

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(6) Outcalt, S. L.; McLinden, M. O. *Ind. Eng. Chem. Res.* **2007**, *46*, 8264–8269.

**Table 1. Densities and Speeds of Sound of Methyl- and Propylcyclohexane Measured in the Density and Sound Speed Analyzer DSA 5000 and Calculated Adiabatic Compressibilities  $\kappa_s = 1/(\rho w^2)^a$** 

temperature $T$ (K)	methylcyclohexane			propylcyclohexane		
	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )	speed of sound $w$ ( $\text{m}\cdot\text{s}^{-1}$ )	adiab. compressibility $\kappa_s$ ( $\text{TPa}^{-1}$ )	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )	speed of sound $w$ ( $\text{m}\cdot\text{s}^{-1}$ )	adiab. compressibility $\kappa_s$ ( $\text{TPa}^{-1}$ )
278.15	782.3	1304.7	750.94	805.4	1371.3	660.26
283.15	778.0	1281.9	782.27	801.5	1349.6	685.01
293.15	769.3	1236.9	849.67	793.7	1307.1	737.38
303.15	760.7	1192.9	923.93	785.9	1265.5	794.47
313.15	751.9	1149.7	1006.1	778.1	1224.7	856.81
323.15	743.1	1107.4	1097.4	770.2	1184.7	925.02
333.15	734.3	1065.6	1199.3	762.3	1145.4	999.94
343.15	725.3	1024.5	1313.6	754.4	1106.9	1081.9

<sup>a</sup> Tabulated values are averages of four replicate tests. The ambient pressure during the measurements was 83 kPa corresponding to the altitude of 1633 m above sea level at Boulder, CO.

**Table 2. Density of Methylcyclohexane Measured in the DMA-HPM Vibrating-Tube Densimeter along Isotherms from 270 to 470 K in Increments of 20 K<sup>a</sup>**

270 K		290 K		310 K		330 K		350 K		370 K	
pressure $p$ (MPa)	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )	pressure $p$ (MPa)	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )	pressure $p$ (MPa)	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )	pressure $p$ (MPa)	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )	pressure $p$ (MPa)	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )	pressure $p$ (MPa)	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )
40.01	814.6	40.00	800.7	40.03	786.3	40.01	772.2	40.00	758.4	40.00	744.7
35.01	811.8	35.00	797.6	35.00	782.9	35.01	768.5	35.00	754.4	34.99	740.4
30.01	808.9	30.00	794.4	30.01	779.4	30.00	764.6	30.01	750.2	30.00	735.8
25.00	805.9	25.00	791.1	25.01	775.7	25.00	760.6	25.00	745.8	25.01	731.0
20.01	802.8	20.01	787.7	20.01	772.0	20.01	756.4	20.00	741.2	19.99	725.8
15.01	799.6	15.00	784.1	15.01	768.0	15.01	752.0	15.01	736.2	15.01	720.3
10.01	796.3	10.00	780.4	10.01	763.8	10.00	747.3	10.01	731.0	10.01	714.3
5.01	792.9	5.00	776.5	5.02	759.4	5.00	742.4	5.00	725.3	5.00	707.9
4.00	792.1	3.99	775.7	4.00	758.5	4.00	741.3	4.01	724.1	4.00	706.5
3.00	791.4	3.01	774.9	3.00	757.6	3.01	740.3	3.01	722.9	3.00	705.1
2.01	790.7	2.00	774.1	2.01	756.7	2.00	739.2	2.00	721.7	2.00	703.7
1.00	790.0	1.00	773.3	1.01	755.7	1.00	738.1	1.00	720.5	0.99	702.2
0.50	789.6	0.50	772.8	0.50	755.2	0.50	737.5	0.50	719.8	0.50	701.4
0.1	789.3	0.1	772.5	0.1	754.8	0.1	737.1	0.1	719.3	0.1	700.8

390 K		410 K		430 K		450 K		470 K	
pressure $p$ (MPa)	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )	pressure $p$ (MPa)	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )	pressure $p$ (MPa)	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )	pressure $p$ (MPa)	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )	pressure $p$ (MPa)	density $\rho$ ( $\text{kg}\cdot\text{m}^{-3}$ )
40.00	731.1	40.00	717.5	40.02	703.9	39.99	690.4	39.99	677.0
35.00	726.3	35.00	712.3	35.00	698.3	35.00	684.2	35.00	670.3
30.00	721.3	30.00	706.8	30.00	692.2	30.00	677.6	30.01	663.1
25.01	716.0	25.00	700.9	25.01	685.7	25.00	670.4	25.01	655.0
20.01	710.2	20.00	694.5	20.00	678.6	20.00	662.4	20.00	646.1
15.00	704.1	15.00	687.5	15.00	670.7	15.00	653.5	15.00	635.9
10.00	697.3	10.01	679.8	10.01	661.8	10.00	643.2	10.00	623.9
5.01	689.9	5.00	671.2	5.00	651.6	5.00	631.1	5.00	609.3
4.00	688.2	4.00	669.3	4.00	649.4	4.00	628.4	4.00	605.9
3.00	686.6	3.00	667.4	3.00	647.1	3.00	625.5	3.00	602.3
2.01	685.0	2.00	665.4	2.00	644.6	2.00	622.5	2.00	598.5
1.00	683.2	1.00	663.3	0.49	640.6	1.00	619.3	1.00	594.3
0.50	682.3	0.51	662.2	0.1	639.6	0.1	616.4	0.1	590.6
0.1	681.6	0.1	661.4						

<sup>a</sup> Values extrapolated to 0.1 MPa are indicated in *italics*.

decrements of 1 MPa to resolve the increasing curvature of the density isotherms as the vapor pressure is approached. This information made it possible to extrapolate the isotherms to ambient pressure. At each temperature, the measured densities at 10 MPa and below were correlated by a quadratic polynomial in pressure from which the density at 0.1 MPa was calculated. These extrapolated density data are given in Tables 2 and 3 in *italics*. They were corroborated by the densities measured with the DSA 5000 instrument at ambient pressure and at temperatures from 278.15 to 343.15 K. Even though this temperature range is only one-third of that covered with the DMA-HPM densimeter, it was found most useful to perform independent measurements in different instruments on the same sample to ensure the mutual

consistency of the experimental and the extrapolated data. The data from the two instruments are compared in the next section.

## 5. Data Correlation and Comparisons

During the measurements and data analysis the experimental results were periodically correlated to monitor the repeatability of the instruments and the consistency of the data. The following two sections report the final correlations for the speed of sound and density results at ambient pressure and for the pressure-dependent densities of the two test liquids. The correlations served as baselines in comparisons of the present results with those of earlier studies and they make the present results immediately usable for engineering and design purposes.

Table 3. Density of Propylcyclohexane Measured in the DMA-HPM Vibrating-Tube Densimeter along Isotherms from 270 to 470 K in Increments of 20 K<sup>a</sup>

270 K		290 K		310 K		330 K		350 K		370 K	
pressure <i>p</i> (MPa)	density $\rho$ (kg·m <sup>-3</sup> )	pressure <i>p</i> (MPa)	density $\rho$ (kg·m <sup>-3</sup> )	pressure <i>p</i> (MPa)	density $\rho$ (kg·m <sup>-3</sup> )	pressure <i>p</i> (MPa)	density $\rho$ (kg·m <sup>-3</sup> )	pressure <i>p</i> (MPa)	density $\rho$ (kg·m <sup>-3</sup> )	pressure <i>p</i> (MPa)	density $\rho$ (kg·m <sup>-3</sup> )
39.96	834.4	40.01	821.5	39.98	807.7	39.99	794.8	40.00	782.2	40.00	769.4
35.01	831.9	35.01	818.7	35.01	804.7	35.00	791.5	35.00	778.6	35.00	765.7
30.00	829.3	30.00	815.9	30.00	801.6	30.00	788.2	30.00	775.0	30.00	761.7
25.00	826.7	25.00	813.0	25.00	798.5	25.00	784.7	25.01	771.2	25.00	757.5
20.00	823.9	20.00	810.0	20.00	795.2	20.00	781.1	20.01	767.2	20.01	753.2
15.00	821.1	15.01	806.8	15.00	791.7	15.01	777.3	15.01	763.0	15.01	748.5
10.00	818.1	10.00	803.5	10.00	788.2	10.00	773.3	10.01	758.5	10.01	743.6
5.01	815.0	5.00	800.0	5.01	784.4	5.00	769.1	5.00	753.8	5.00	738.3
4.00	814.4	4.01	799.3	4.00	783.6	3.99	768.2	4.00	752.9	4.00	737.2
2.99	813.7	3.00	798.6	3.00	782.8	3.00	767.3	3.00	751.9	3.00	736.0
2.00	813.0	2.01	797.8	2.01	782.0	2.00	766.4	1.99	750.8	2.01	734.9
1.00	812.4	1.00	797.1	1.00	781.2	1.00	765.5	1.00	749.8	1.01	733.7
0.50	812.0	0.51	796.7	0.51	780.8	0.50	765.1	0.50	749.3	0.50	733.1
0.1	811.8	0.1	796.4	0.1	780.5	0.1	764.7	0.1	748.9	0.1	732.6

390 K		410 K		430 K		450 K		470 K	
pressure <i>p</i> (MPa)	density $\rho$ (kg·m <sup>-3</sup> )	pressure <i>p</i> (MPa)	density $\rho$ (kg·m <sup>-3</sup> )	pressure <i>p</i> (MPa)	density $\rho$ (kg·m <sup>-3</sup> )	pressure <i>p</i> (MPa)	density $\rho$ (kg·m <sup>-3</sup> )	pressure <i>p</i> (MPa)	density $\rho$ (kg·m <sup>-3</sup> )
39.99	756.9	40.00	744.4	40.00	732.0	39.99	719.6	40.00	707.4
35.00	752.8	35.01	740.0	35.00	727.2	35.01	714.4	35.00	701.8
30.00	748.5	30.00	735.3	30.01	722.1	30.01	708.8	30.00	695.7
25.00	744.0	25.00	730.3	25.00	716.6	25.01	702.9	25.00	689.2
20.00	739.1	20.00	725.0	20.00	710.7	20.00	696.4	20.00	682.0
15.00	734.0	15.00	719.3	15.01	704.4	15.01	689.3	14.99	674.1
10.01	728.5	10.01	713.1	10.01	697.4	10.00	681.4	10.01	665.2
5.00	722.5	5.01	706.3	5.00	689.7	5.00	672.5	5.00	654.9
4.00	721.2	4.00	704.8	3.99	688.0	4.00	670.6	4.00	652.6
3.00	719.9	2.99	703.3	3.00	686.3	3.00	668.6	3.00	650.2
2.01	718.6	2.01	701.9	1.99	684.5	1.99	666.5	2.00	647.8
1.00	717.3	0.99	700.3	1.00	682.7	1.00	664.4	0.99	645.2
0.50	716.6	0.51	699.5	0.52	681.8	0.51	663.3	0.50	643.9
0.1	716.1	0.1	698.9	0.1	681.1	0.1	662.4	0.1	642.8

<sup>a</sup> Values extrapolated to 0.1 MPa are indicated in *italics*.

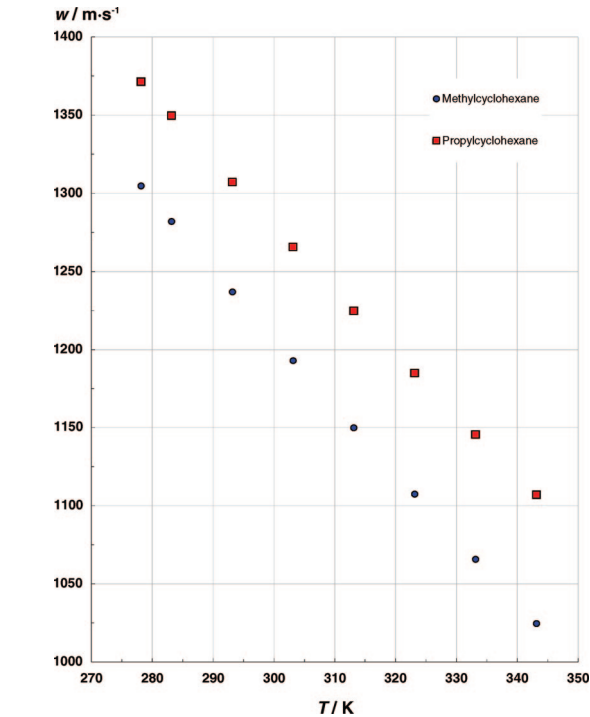


Figure 2. Measured speed of sound data of methyl- and propylcyclohexane as a function of temperature at ambient pressure.

Nonlinear least-squares regressions were performed with the Solver tool in Microsoft Excel to obtain the correlation parameters. Since Solver provides no statistical measures of the adjustable parameters, the macros by de Levie<sup>7</sup> were used to

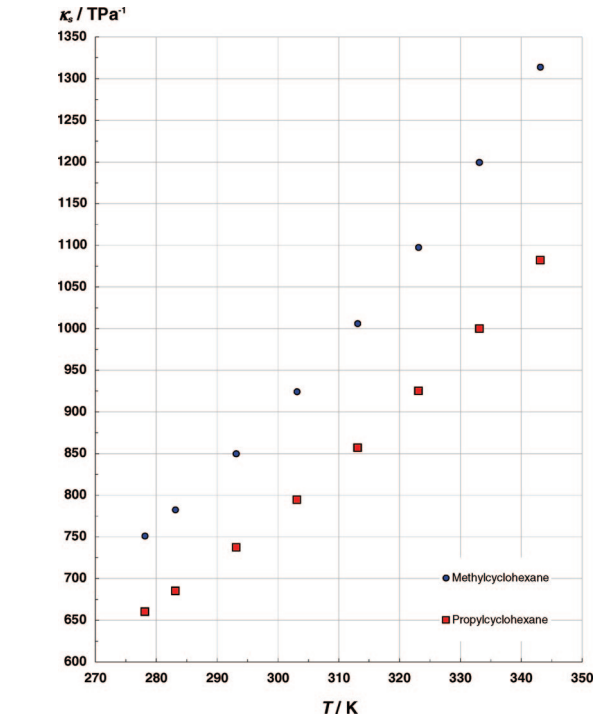


Figure 3. Measured adiabatic compressibility of methyl- and propylcyclohexane as a function of temperature at ambient pressure.

obtain these indicators for the quality of the fits. In using Microsoft Excel, special attention was paid to its limited internal numerical precision.<sup>8,9</sup> To ensure that no numerical losses



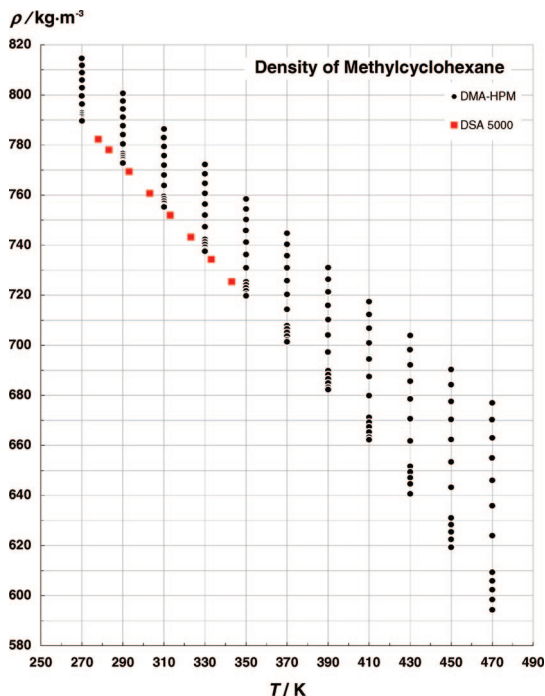


Figure 4. Measured density data of methylcyclohexane as a function of temperature with pressures up to 40 MPa.

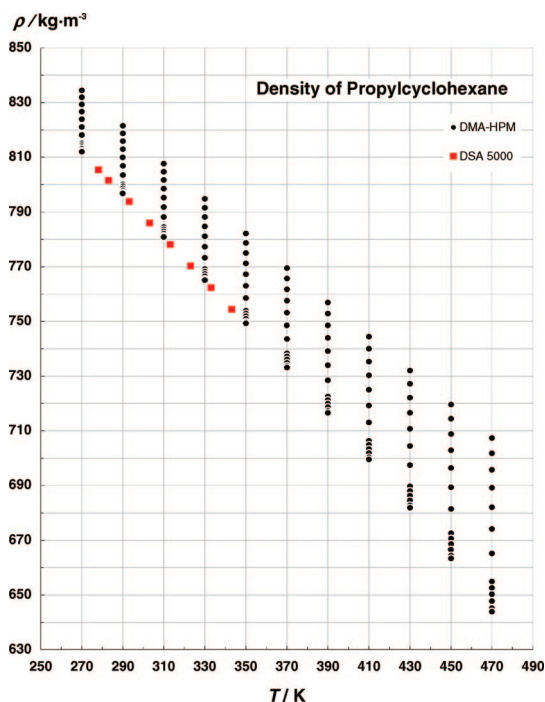


Figure 5. Measured density data of propylcyclohexane as a function of temperature with pressures up to 40 MPa.

occurred, the final correlations were programmed in FORTRAN and compared with the Excel calculations.

**5.1. Properties at Ambient Pressure.** The speed of sound data at atmospheric pressure were correlated as a function of temperature with the empirically modified Rackett equation<sup>10</sup>

$$w = \beta_1 \beta_2^{-(1+(1-T/\beta_3)^{\beta_4})} \quad (1)$$

(7) de Levie, R. *Advanced Excel for scientific data analysis*; Oxford University Press: Oxford, 2004.

(8) McCullough, B. D.; Wilson, B. *Comp. Stats. Data Anal.* **1999**, *31*, 27–37.

(9) de Levie, R. *Am. J. Phys.* **2007**, *75*, 619–628.

(10) Rackett, H. G. *J. Chem. Eng. Data* **1970**, *15*, 514–517.

Table 4. Parameters of the Correlations for the Speed of Sound of Methyl- and Propylcyclohexane at Ambient Pressure and Temperatures from 278.15 to 343.15 K<sup>a</sup>

parameter	methylcyclohexane		propylcyclohexane	
	value	std dev	value	std dev
$\beta_1$ (m·s <sup>-1</sup> )	86.575 000	0.101	101.532 70	0.13
$\beta_2$	0.169 281 93	$9.6 \times 10^{-5}$	0.183 683 89	$1.1 \times 10^{-4}$
$\beta_3$ (K)	466.811 56	0.080	495.491 40	0.11
$\beta_4$	0.706 560 79	$1.5 \times 10^{-4}$	0.756 401 76	$1.5 \times 10^{-4}$
AAD (%)		$5.6 \times 10^{-3}$		$3.4 \times 10^{-3}$
rms (%)		$3.0 \times 10^{-4}$		$1.2 \times 10^{-4}$

<sup>a</sup> Average absolute deviations and residual mean squares deviations are given in percent to indicate the quality of the correlations.

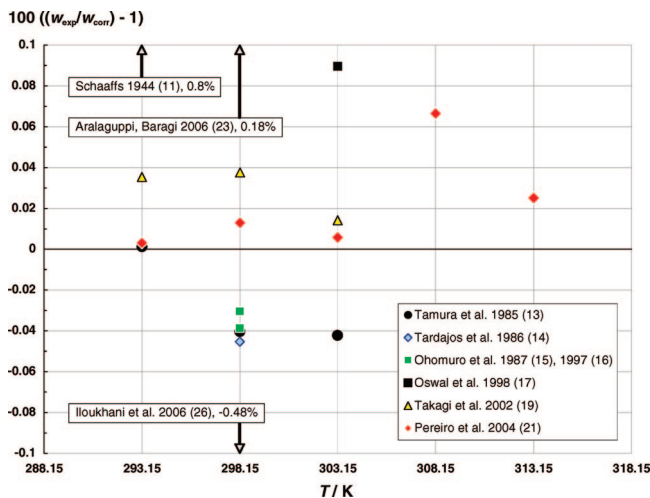


Figure 6. Deviations of literature speed of sound data of methylcyclohexane at ambient pressure from the Rackett correlation, eq 1.

Table 5. Parameters of the Rackett Correlations for the Density of Methyl- and Propylcyclohexane at Ambient Pressure and Temperatures from 270 to 470 K

parameter	methylcyclohexane		propylcyclohexane	
	value	std dev	value	std dev
$\beta_5$ (kg·m <sup>-3</sup> )	199.471 15	0.044	270.958 67	0.054
$\beta_6$	0.448 000 08	$4.8 \times 10^{-5}$	0.517 142 48	$5.1 \times 10^{-5}$
$\beta_7$ (K)	528.827 18	0.017	550.747 23	0.032
$\beta_8$	0.474 991 56	$6.8 \times 10^{-5}$	0.607 998 05	$7.9 \times 10^{-5}$

The symbol  $w$  denotes the speed of sound in units of meters per second, and  $T$  is the absolute temperature in kelvin. The values of the adjustable parameters  $\beta_1$ – $\beta_4$  and their standard deviations are listed in Table 4 for both test liquids. While the Rackett equation was originally proposed and is often used to correlate density data, it was applied here to the speed of sound data as well for reasons of uniformity and good extrapolation behavior beyond the temperature range of the experimental data (278.15–343.15 K). The experimental speed of sound data for both liquids are represented by the correlation within their estimated uncertainty.

While the speed of sound of propylcyclohexane appears not to have been measured previously, a number of literature data exist for the speed of sound of methylcyclohexane,<sup>11–26</sup> although they are limited to the temperature range from 293.15 to 313.15

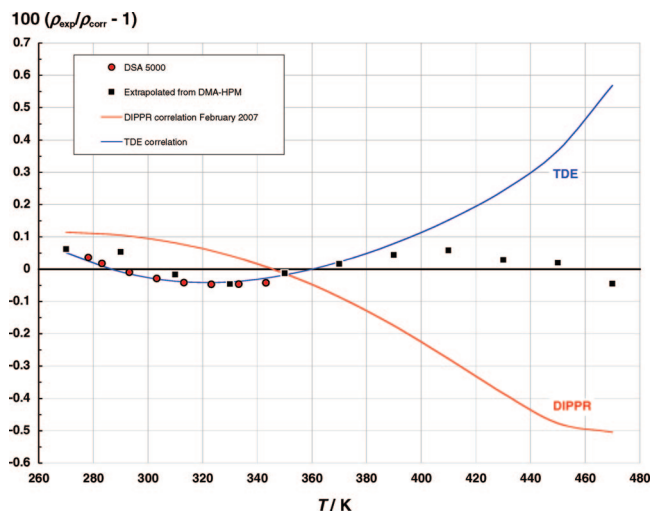
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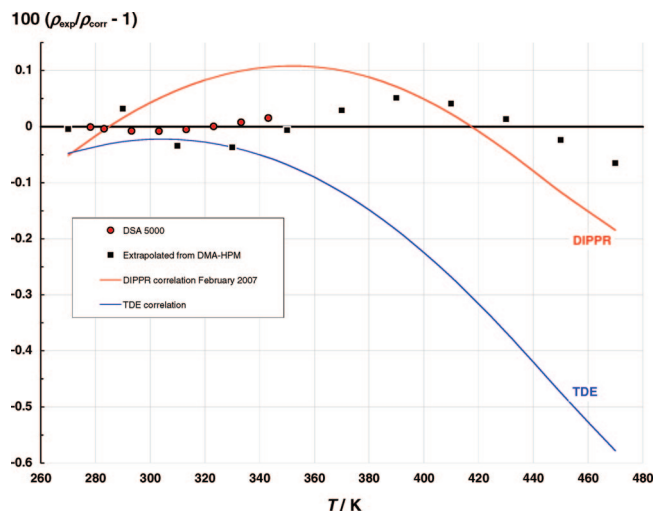
**Figure 7.** Deviations of density data of methylcyclohexane at ambient pressure from the Rackett correlation, eq 2.

K. Omitting repeat publications of identical data, the literature values are compared with the present correlation in Figure 6. The majority of the deviations range between  $-0.05\%$  and  $0.07\%$  which is well within the experimental uncertainty of the present results. Note that Pereiro et al.<sup>21</sup> measured with the same type of instrument as was used in the present work but did not exploit its full temperature range although this would have been only a matter of programming the device.

When applied to the combined density data at ambient pressure in the temperature range 270 to 470 K, the Rackett equation is written as

$$\rho = \beta_5 \beta_6^{-(1+(1-T/\beta_7)^{\beta_8})} \quad (2)$$

The symbol  $\rho$  denotes the density in units of kilograms per cubic meter. The parameter values  $\beta_5$ – $\beta_8$  and their standard deviations are listed in Table 5 for both test liquids. Comparisons of the present measurement results relative to this correlation are shown in the deviation plots Figure 7 for methylcyclohexane and Figure 8 for propylcyclohexane. For both compounds, the experimental results from the DSA 5000 and the ambient pressure values extrapolated from the results of the DMA-HPM densimeter are represented by the correlations to within  $\pm 0.05\%$  over the temperature range 270–470 K. In the overlapping temperature range 278.15–343.15 K, the mutual agreement between the results from the DSA 5000 and the extrapolated values is within 0.02%, with the exception of the extrapolated values at 290 K,



**Figure 8.** Deviations of density data of propylcyclohexane at ambient pressure from the Rackett correlation, eq 2.

which are 0.05% higher than the experimental densities from the DSA 5000. Overall, the agreement between the independently determined data sets from the two densimeters is satisfactory and consistent with their respective estimated experimental uncertainties.

The present results were also compared with literature density data for the two test liquids. Instead of tracing and compiling data from individual references, the comparisons were made with correlations for the density of the test liquids in two widely used databases. Their contents indicate that the properties of methylcyclohexane have been measured more often than those of propylcyclohexane. The DIPPR database<sup>27</sup> reports density correlations at ambient pressure in the form of eq 2 based on evaluated literature data. The temperature range of the correlation for the density of methylcyclohexane is 146.58–572.10 K, with experimental data coverage up to 372 K. The correlation for propylcyclohexane is applicable from 176.25 to 639.15 K, with the underlying experimental data reaching up to 383 K.

The second database consulted in this work is the NIST ThermoData Engine (TDE), version 2.0.<sup>28</sup> This database returned correlations of a different form than eq 2 for the saturated liquid densities of the two test compounds. The correlation for methylcyclohexane was rated for a temperature range from 146.591 to 572.223 K and that for propylcyclohexane for the range 178.262–630.8 K.

Including these correlations in the comparison for methylcyclohexane, Figure 7 shows that the TDE correlation agrees with the densities of this work closely up to 370 K but gives systematically higher values at higher temperatures, with a maximum deviation of 0.6% at 470 K. The structurally different Rackett correlation in the DIPPR database yields slightly higher densities than the present results up to 350 K, at which temperature it returns the same density as the TDE correlation. With increasing temperature, the DIPPR correlation yields systematically lower densities than the present study, reaching a minimum of  $-0.5\%$  at 470 K. The results of this work confirm the TDE correlation below 390

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**Table 6. Parameters of the Tait Correlations for the Density of Methyl- and Propylcyclohexane in Terms of Temperature and Pressure**

parameter	methylcyclohexane		propylcyclohexane	
	value	std dev	value	std dev
$\beta_9$	$75.274617 \times 10^{-3}$	$8.9 \times 10^{-4}$	$58.350428 \times 10^{-3}$	$9.5 \times 10^{-4}$
$\beta_{10}$	$-2.1885588 \times 10^{-3}$	$1.2 \times 10^{-3}$	$6.6897957 \times 10^{-3}$	$1.4 \times 10^{-3}$
$\beta_{11}$	$4.2445614 \times 10^{-3}$	$5.0 \times 10^{-4}$	$5.4186171 \times 10^{-3}$	$5.8 \times 10^{-4}$
$\beta_{12}$	273.96987	1.8	252.66430	2.1
$\beta_{13}$	-257.88011	2.0	-217.84382	2.3
$\beta_{14}$	61.119164	0.56	48.450168	0.65

K and provides data, that will allow improvement of both databases to higher temperatures.

The comparison for propylcyclohexane in Figure 8 reveals a different pattern of deviations. Here, the correlations from DIPPR and TDE coincide at about 271 K and diverge from that point as temperature increases. While the deviations of both correlations run somewhat parallel with similar curvature, the DIPPR correlation yields densities within 0.1% and -0.2% of the present results, whereas densities calculated with the TDE correlation are systematically lower, with a maximum negative deviation of -0.6% at 470 K.

**5.2. Pressure Dependence.** The pressure and temperature dependence of the measured densities of each test liquid were correlated with the modified Tait equation<sup>29</sup>

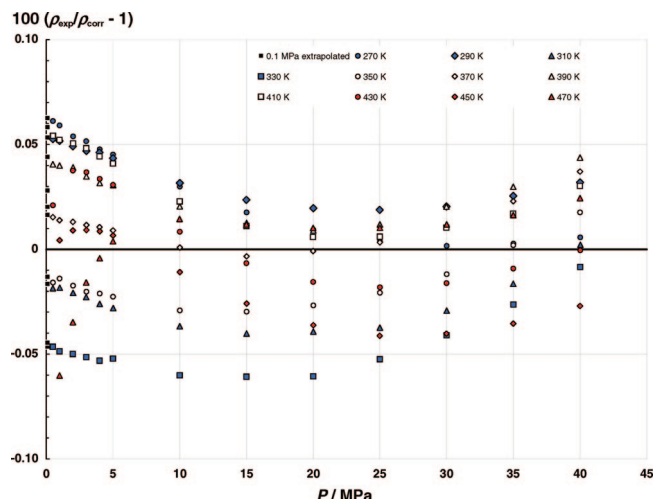
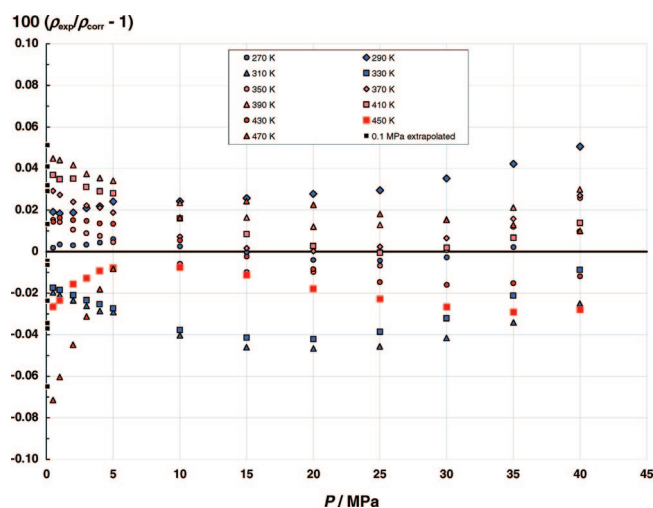
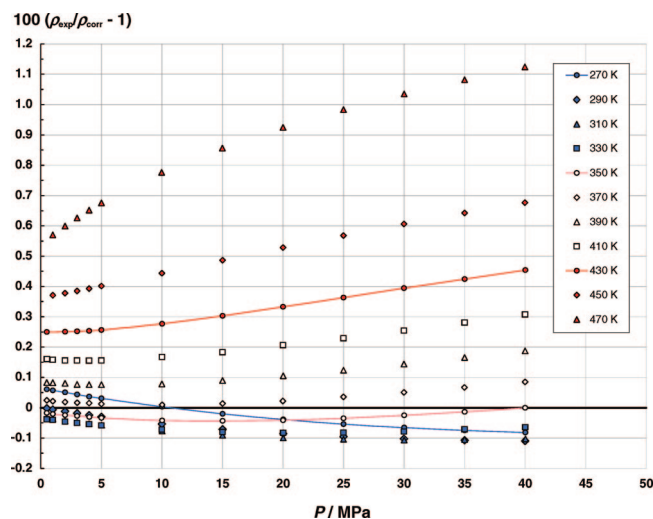
$$\rho(T, p) = \frac{\rho_{\text{ref}}(T, p_{\text{ref}})}{1 - C(T) \ln \left( \frac{p + B(T)}{\rho_{\text{ref}} + B(T)} \right)} \quad (3)$$

where  $p$  denotes pressure and  $\rho_{\text{ref}}(T)$  is the temperature-dependent density at the reference pressure  $p_{\text{ref}} = 0.1$  MPa, as given in eq 2 with the parameter values in Table 5. To account for the wide temperature range of the measurements in this work, a temperature dependence of the Tait parameters  $B(T)$  and  $C(T)$  was introduced by quadratic polynomials,

$$C(T) = \beta_9 + \beta_{10}T_r + \beta_{11}T_r^2 \quad \text{and} \quad B(T) = \beta_{12} + \beta_{13}T_r + \beta_{14}T_r^2 \quad (4)$$

where  $T_r$  is the absolute temperature  $T$  divided by 273.15 K. The parameter values and their standard deviations are listed in Table 6. Relative deviations between measured densities and those calculated with the correlating eqs 2 and 3 are displayed in Figure 9 for methylcyclohexane and in Figure 10 for propylcyclohexane. The correlations represent the experimental data within  $\pm 0.06\%$ .

While the pressure dependence of the density of propylcyclohexane has not been measured before, it is possible to compare the measured densities of methylcyclohexane with literature data. These were compiled and evaluated in the review of Cibulka and Tagaki<sup>30</sup> who established a Tait equation similar to eq 3 for the temperature range 203 to 523.15 K with pressures up to 500 MPa. Figure 11 illustrates the deviations of the Tait equation of Cibulka and Tagaki<sup>30</sup> from the correlation developed in this work, eqs 2 and 3, at the experimental pressures in Table 2. Thus, Figures 9 and 11 have the same baseline. In Figure 11, densities on the isotherms below 390 K show agreement within the estimated experimental uncertainty of the measurement results reported here. At pressures above 20 MPa at 390 K and at all higher temperatures, the correlation of Cibulka and Tagaki yields

**Figure 9.** Deviations of all measured density data of methylcyclohexane from the modified Tait correlation, eq 3.**Figure 10.** Deviations of all measured density data of propylcyclohexane from the modified Tait correlation, eq 3.**Figure 11.** Comparison of the present density data of methylcyclohexane with the correlation of Cibulka and Takagi.<sup>30</sup> Points along selected isotherms are connected to improve the legibility of the graph.

systematically higher densities, reaching a maximum deviation of 1.1% at 470 K and 40 MPa. The deviations with increasing pressure result most likely from the fact that

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Cibulka and Tagaki based their correlation above 392 K only on the data of Kerimov and Agaev,<sup>31</sup> with a maximum pressure of 4 MPa. The increasing deviations at the lowest pressures with a maximum of 0.55% at 470 K indicate a systematic disagreement in the temperature dependence between the data of Kerimov and Agaev and the present measurements. Further measurements are needed to resolve the disagreement.

Since the review of Cibulka and Takagi was published in 1999, additional density measurements of methylcyclohexane were reported by Zéberg-Mikkelsen et al. in 2002,<sup>32</sup> identically republished but in the context of a different mixture in 2003.<sup>33</sup> These data were measured in the temperature range 293.15–353.15 K, with pressures up to 60 MPa and extrapolated to 100 MPa. Figure 12 illustrates deviations of this data set from the correlation presented here, again using the same baseline as in Figures 9 and 11. The agreement is within the estimated experimental uncertainty of the measurements reported here.

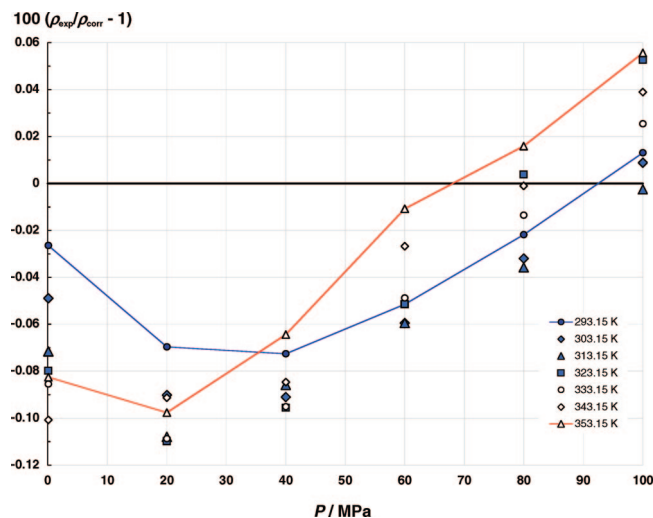
## 6. Conclusions

New measurements are reported for the speed of sound and the density of methylcyclohexane and propylcyclohexane. The speed of sound was measured at ambient pressure from 278.15 to 343.15 K. Densities were measured independently in two vibrating-tube densimeters in the combined range of temperatures from 270 to 470 K, with pressures from ambient to 40 MPa. For the density of methylcyclohexane, the region from 390 to 470 K with pressures above 4 MPa has been measured for the first time. The present results agree with most literature data in the overlapping range of states within their estimated uncertainty. However, one literature data set deviates systematically in the temperature dependence of the low-pressure density above 390 K. Future measurements should focus on this region.

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**Figure 12.** Comparison of the present density data of methylcyclohexane with the experimental results of Zéberg-Mikkelsen et al.<sup>32</sup> Points along the isotherms with the lowest and the highest temperature are connected to improve the legibility of the graph.

The pressure dependence of the density of propylcyclohexane has not been measured before.

While the molecular structures of the two test compounds differ by only a  $-\text{CH}_2-\text{CH}_2-$  group in the aliphatic side chain, their macroscopic properties exhibit distinct differences. The adiabatic compressibility, derived from the measured speed of sound and density at ambient pressure, was found among the three properties the most sensitive to the differences on the molecular scale.

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