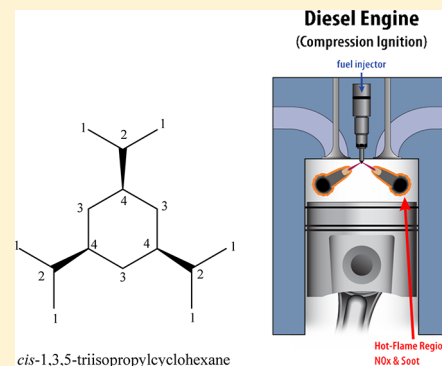# Chemical and Thermophysical Characterization of 1,3,5-Triisopropylcyclohexane

Thomas J. Bruno,* Tara J. Fortin, Tara M. Lovestead, and Jason A. Widegren

Thermophysical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305, United States

ABSTRACT: The complex nature of finished fuels makes definitive studies on composition and combustion properties very difficult and uncertain. This has led to the adoption of fuel surrogate mixtures in such studies. The development of a surrogate mixture is itself a nontrivial process, and a surrogate mixture is often developed specifically for a given purpose. Often, thermophysical property surrogate mixtures cannot be used for examination of combustion properties, and vice versa. Surrogates range in complexity from a single component to complex mixtures containing 20 or more components. A recent study on surrogate mixture development for diesel fuel used state-of-the-art techniques of ^{13}C and ^{1}H nuclear magnetic resonance (NMR) spectroscopy and the advanced distillation curve to characterize fuel composition and volatility, respectively. This work indicated the need for a multiply substituted, low cetane number, high molecular mass monocycloalkane surrogate mixture component. The addition of 1,3,5-triisopropylcyclohexane as a palette component was chosen to serve this need. Before this component can be used in any modeling or experimental effort, we first require some basic chemical and thermophysical properties. In this paper, we present chemical characterization results from gas chromatography with mass spectrometry, ^{13}C NMR spectrometry, isothermal Kovats' retention indices at (150 to 225) °C (on 5 % phenyl-95 %-dimethyl polysiloxane), and refractive indices at (20, 25, and 30) °C. We also present ambient pressure thermophysical property measurements: density, speed of sound, and derived adiabatic compressibility from (5 to 70) °C and kinematic viscosity from (20 to 100) °C. These properties and characterization parameters are critical to the successful application of 1,3,5-triisopropylcyclohexane in experimental and modeling studies of surrogate diesel fuels.

cis-1,3,5-triisopropylcyclohexane

INTRODUCTION

Over the last several years, the scientific and engineering communities have been searching for appropriate fuel surrogates to represent real fuels such as diesel fuel (ultralow sulfur diesel fuel, ULSD), aviation turbine kerosene (Jet-A, JP-8, etc.), and rocket propellant (RP-1, RP-2, etc.). The need for useful surrogates (simpler stand-in mixtures that are more easily characterized) was highlighted in a workshop on real transportation fuels that was held in 2003, resulting in the formation of three working groups in 2004 (one each to develop surrogates for gasolines, diesel fuels, and aviation fuels) and in additional workshops.[1-3] The critical needs were subsequently reiterated in each Multi-Agency Coordinating Committee on Combustion Research (MACCCR) Fuel Summit that was held between 2009 and 2011.[4] For some fuels, such as gasolines, reference fluid mixtures have been developed as consensus standards upon which scientists and engineers can develop and perform thermophysical, kinetic, and engineering property measurements.[5] Kerosene fuels are more diverse, however, and consensus on a detailed set of specifications is simply more difficult to achieve. This is partially because the requirements of testing protocols for turbine fuels and the required knowledge base for some of the components of the real fuel (such as detailed kinetic mechanisms) are often absent. It is also partially because

different technical communities have different uses and targets for surrogates.

The resulting approach that has been adopted is to test and model surrogate fluids instead of multiple samples of the finished fuel.[6-10] An inherent limitation of this approach is that surrogate mixtures often must be developed for specific applications, such as the simulation of chemical kinetic phenomena (oxidation, combustion, soot formation, emissions, etc.) and physical properties (density, volatility, fuel spray effects, drop size distributions, etc.).[11,12] These surrogates range in complexity from those as simple as a single component to mixtures of 20 or more components. While single component surrogates may be adequate for simple applications, such as assessing combustion efficiency, more complex, multicomponent surrogate mixtures are sometimes required for measurements and studies that are very dependent upon fuel chemistry components.

A recent study by a multidisciplinary team (from 10 institutions) on surrogate mixture development for diesel fuel made use of state-of-the-art techniques including ^{13}C and ^{1}H nuclear magnetic resonance (NMR) spectroscopy and the

ACS Publications
2343
dx.doi.org/10.1021/je3005479 | J. Chem. Eng. Data 2012, 57, 2343–2349

advanced distillation curve to characterize fuel composition and volatility, respectively.[13] The goal was a methodology for creating surrogate diesel fuels with improved fidelity in matching the molecular structures, ignition quality, and volatility characteristics of the respective target diesel fuels. This work resulted in an initial surrogate mixture that did indeed represent many properties within the desired uncertainty. The work also indicated, however, the need for a multiply substituted, low cetane number, high molecular mass monocycloalkane surrogate mixture component. Careful consideration of potential components that could meet these needs led to selection of 1,3,5-triisopropylcyclohexane, a fluid that is not available commercially as an industrial or as a research chemical. Before this or any chemical can be evaluated as a surrogate component, it must first be synthesized and characterized. In this paper, we report some chemical and thermophysical property characterization measurements on this fluid.

EXPERIMENTAL SECTION

The fluid of interest, 1,3,5-triisopropylcyclohexane, is not available commercially and was obtained from a custom synthesis laboratory.[14,15] Synthesis was done by catalytic hydrogenation of the corresponding substituted aromatic ring compound, 1,3,5-triisopropylbenzene. The product was purified by washes with potassium hydroxide and sulfuric acid, followed by drying and heating with sodium metal. The sample was clear and appeared to have the consistency of syrup. The odor was slight, consistent with the relatively high molecular mass and low vapor pressure. The purified product was initially analyzed by gas chromatography (by the custom synthesis laboratory) and showed two geometrical isomers with area counts in the ratio 88 % to 12 % (with an uncertainty of 1 %). The major product was assigned to the e,e,e-geometry (cis-, cis-, cis-, or all cis-) and the minor product to the e,e,a-geometry (cis-, cis-, trans-) of the substituents around the cyclohexane ring. The all-equatorial e,e,e-geometry isomer (all cis-) is expected to be thermodynamically more stable, with an approximate equilibrium constant (at ambient temperature) of 88/12 = 7.3. In other work, the derived cetane number (DCN) of this fluid was determined to be 25.3.[16]

For clarity in the remainder of our discussion, since we use a relatively large variety of techniques, we will include the experimental details of each measurement technique with the description of the results.

RESULTS AND DISCUSSION

Analysis by Gas Chromatography–Mass Spectrometry. The sample was analyzed by use of gas chromatography (GC) with mass spectrometric (MS) detection for several important purposes. First, we required a check on the purity of the fluid upon which all measurements would be performed. Second, since this fluid has not been examined previously, it is important to provide the chromatographic and mass spectral information to the fuel science community in particular and the scientific community at large.

The GC was done on a commercial instrument with a 30 m capillary column of 5 % phenyl-95 %-dimethyl polysiloxane having a thickness of 1.0 μm and an internal diameter of 0.25 μm. The sample (0.1 μL) was injected manually via chromatographic syringe into a split/splitless injector set with a 200:1 split ratio. No solvent was used. The injector was
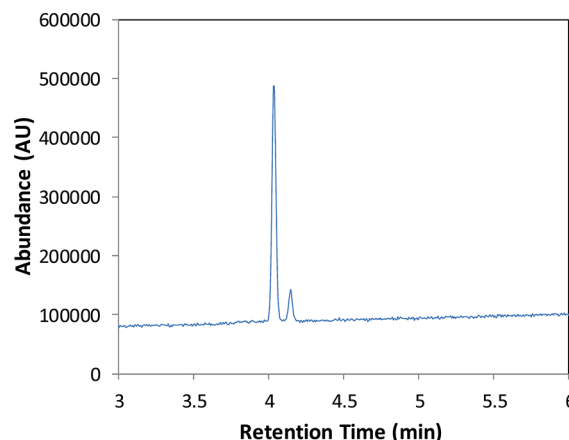

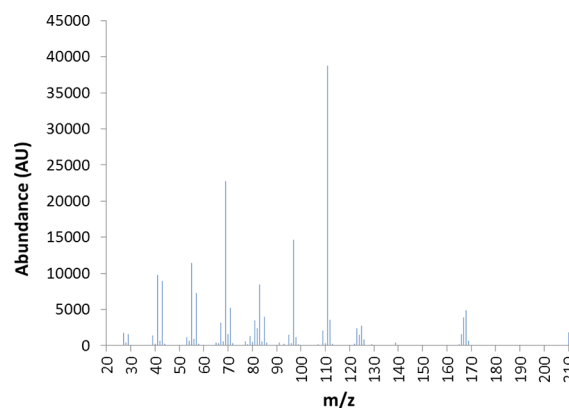**Figure 1.** Total ion chromatogram of 1,3,5-triisopropylcyclohexane. Conditions are described in the text.

Figure 2. Mass spectrum of 1,3,5-triisopropylcyclohexane. Conditions are discussed in the text.
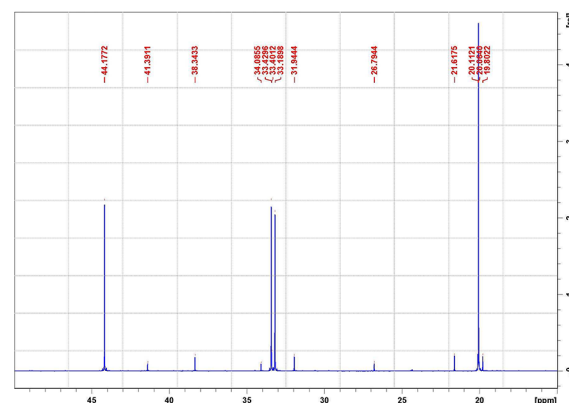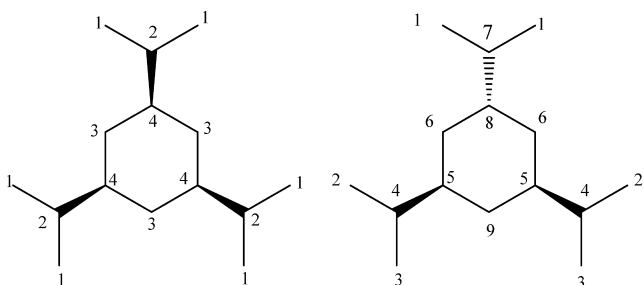

Figure 3. [13]C spectra of 1,3,5-triisopropylcyclohexane obtained by use of a 600 MHz NMR. The conditions and uncertainties are discussed in the text.

operated at a temperature of 200 °C and a constant (gauge) head pressure of 68.9 kPa (10 psig). A column temperature ramp from (200 to 225) °C at 4 °C·min^{-1} was used. Mass spectra were collected for each chromatographic peak from (15 to 550) relative molecular mass (RMM) units. Spectra on this fluid are not contained in the National Institute of Standards and Technology (NIST) mass spectral database. Therefore, mass spectral peaks were interpreted manually.[17,18]

Figure 4. The e,e,e-geometry and e,e,a-geometry isomers of 1,3,5-triisopropylcyclohexane, with the magnetically equivalent carbons indicated numerically. Four of the ^{13}C NMR spectral peaks correspond to the four unique carbons on the e,e,e-geometry isomer, and nine of the peaks correspond to the nine unique carbons on the e,e,a-geometry isomer.

Table 1. [13]C Spectral Information for 1,3,5-Triisopropylcyclohexane Obtained with a 600 MHz NMR[a]

peak(s)/ppm	relative integral area
44.18	3.000
41.39	0.126
38.34	0.249
34.09	0.115
33.43 + 33.40 + 33.19[b]	6.250
31.94	0.245
26.79	0.115
21.62	0.243
20.11 + 20.06 + 19.80[b]	6.510

[a]The uncertainty is discussed in the text. [b]These peaks were integrated together because of poor separation.

Table 2. Kovats' Retention Index (I) as a Function of Temperature (T/°C)[a]

T/°C	Kovats' retention index (I)	coefficients for eq 2	
	(a) e,e,e-1,3,5-Triisopropylcyclohexane		
150	1376.2 (1.5)	A	1294.147
175	1384.0 (1.2)	B	−23902.937
200	1393.1 (1.3)	C	−441.280
225	1404.7 (1.1)	MSE	0.035
δI_{sample}/10 °C	0.38		
	(b) e,e,a-1,3,5-Triisopropylcyclohexane		
150	1382.9 (1.6)	A	1267.860
175	1394.1 (1.3)	B	−35273.393
200	1405.2 (1.3)	C	−455.875
225	1420.8 (1.1)	MSE	0.178
δI_{sample}/10 °C	0.50		

[a]The expanded uncertainty with a coverage factor $k = 2$ is provided parenthetically. MSE is the mean squared error for the measured I compared with the calculated I obtained by the use of eq 2.

Only two chromatographic peaks were observed in the total ion chromatogram; one peak at a retention time (RT) of 4.04 min and one peak at RT = 4.15 min. Baseline resolution was achieved for the peak separation, as seen in Figure 1. The raw uncalibrated peak areas were determined. The average raw uncalibrated peak areas for three injections were 88.7 % for the first peak and 11.3 % for the second peak. The uncertainty in these peak areas was 0.2 %. We note inter alia that this analysis is in agreement, within experimental uncertainty, with that

Table 3. Refractive Indices (n_D) of 1,3,5-Triisopropylcyclohexane at Three Different Temperatures (T/°C)[a]

T/°C	n_D
20	1.4571 (0.0004)
25	1.4547 (0.0003)
30	1.4525 (0.0005)

[a]The expanded uncertainty with a coverage factor $k = 2$ is provided in the parentheses. Note that these measurements are for the equilibrium mixture of the two geometrical isomers.

performed by the custom synthesis laboratory that provided the fluid. The mass spectrum (for the larger of the two peaks) is shown in Figure 2. Although only one spectrum is shown, the spectrum for the smaller chromatographic peak is essentially indistinguishable from that of the larger peak. Fragments are observed for ions consistent with 1,3-diisopropylcyclohexane (RMM = 168.2) and isopropylcyclohexane (RMM = 126.1).

Furthermore, the mass fragmentation patterns indicate that ring-opening reactions were noted, generating smaller molecular mass ions and radicals. For example, the very large peak at m/z at 111 is consistent with a C_8H_{15} radical, and the peaks at m/z = 69.1, 141.1, and 57.0 might indicate that 1,3,5-triisopropylcyclohexane and isopropylcyclohexane lose a C_5H_9 radical (RMM = 69.1). Additionally, compounds such as ethylene (RMM = 28.0), a C_3H_5 radical (RMM = 41.0), a C_3H_7 radical (RMM = 43.1), a C_4H_7 radical (RMM = 55.1), a C_4H_9 radical (RMM = 57.1), a C_6H_{11} radical (RMM = 83.1), and a C_7H_{13} radical (RMM = 97.1) were observed in high abundance.

NMR Spectrometry. To further characterize the sample of 1,3,5-triisopropylcyclohexane, we utilized a 600 MHz NMR spectrometer (operated at 150.9 MHz for ^{13}C) to obtain a quantitative ^{13}C spectrum (see Figure 3).[19] The NMR sample was prepared by dissolving approximately 50 mg of the 1,3,5-triisopropylcyclohexane in 1 g of deuterated chloroform ($CDCl_3$). The sample was maintained at 30 °C for the NMR measurement. Quantitative peak integrals were obtained by use of inverse-gated waltz-16 proton decoupling, a long interpulse delay (2.4 s acquisition time, 50 s relaxation delay), and a 30° flip angle. The spectrum in Figure 3, which is the result of 4432 scans, is referenced to the solvent resonance at 77.23 ppm. A sweep width of 15121.0 Hz (0 ppm to 100 ppm) was used, but only the region from 15 ppm to 50 ppm is shown in Figure 3.
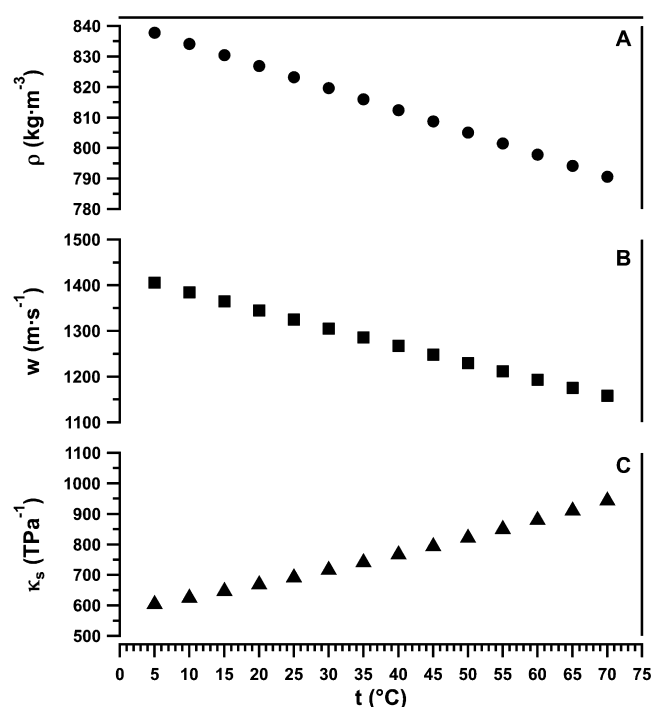
The e,e,e-geometry and e,e,a-geometry isomers of 1,3,5-triisopropylcyclohexane (Figure 4) are easily distinguished by ^{13}C NMR. The e,e,e-geometry isomer is expected to have four peaks with relative area ratios of 6:3:3:3. The e,e,a-geometry isomer is less symmetric and is expected to have nine peaks with relative area ratios of 2:2:2:2:2:2:1:1:1. In fact, the spectrum in Figure 3 shows four larger peaks for the e,e,e-geometry isomer at 20.06 ppm, 33.19 ppm, 33.43 ppm, and 44.18 ppm. It also shows nine smaller peaks for the e,e,a-geometry isomer at 19.80 ppm, 20.11 ppm (a shoulder on the larger peak at 20.06 ppm), 21.62 ppm, 26.79 ppm, 31.94 ppm, 33.40 ppm (a shoulder on the larger peak at 33.43 ppm), 34.09 ppm, 38.34 ppm, and 41.39 ppm. The peak areas are reported in Table 1.

We note that some of the peaks are not well-separated; such peaks were integrated together, and it is the combined integral that is reported in Table 1. Importantly, the expected peak area ratios (based upon the GC-MS data reported above, and the measurements done at the custom synthesis laboratory

Table 4. Measured Densities (ρ/kg·m⁻³), Speeds of Sound (w/m·s⁻¹), and Derived Adiabatic Compressibilities (κ_s/T·Pa⁻¹) for 1,3,5-Triisopropylcyclohexane (Mixture of e,e,e- and e,e,a Isomers) at Approximately 83 kPa (1650 m above Sea Level)[a]

T/°C	ρ/kg·m⁻³	$U(\rho)$/kg·m⁻³	w/m·s⁻¹	$U(w)$/m·s⁻¹	κ_s/T·Pa⁻¹	$U(\kappa_s)$/T·Pa⁻¹
5.00	837.78	0.07	1405.7	0.5	604.1	0.2
10.00	834.14	0.07	1385.0	0.5	625.0	0.2
15.00	830.52	0.07	1364.8	0.5	646.5	0.2
20.00	826.89	0.07	1344.8	0.5	668.7	0.2
25.00	823.27	0.07	1325.0	0.5	691.8	0.2
30.00	819.64	0.07	1305.5	0.5	715.8	0.3
35.00	816.02	0.07	1286.3	0.5	740.6	0.3
40.00	812.39	0.07	1267.3	0.5	766.4	0.3
45.00	808.76	0.07	1248.6	0.5	793.2	0.3
50.00	805.12	0.07	1230.0	0.5	820.9	0.3
55.00	801.49	0.07	1211.7	0.5	849.8	0.3
60.00	797.85	0.07	1193.6	0.5	879.8	0.3
65.00	794.21	0.07	1175.6	0.5	911.0	0.4
70.00	790.57	0.07	1158.0	0.5	943.3	0.4

[a]The expanded uncertainties with a coverage factor k = 2 are also provided. Note that these measurements are for the equilibrium mixture of the two geometrical isomers.

Figure 5. Density (A), speed of sound (B), and adiabatic compressibility (C) as a function of temperature for 1,3,5-triisopropylcyclohexane at approximately 83 kPa (1650 m above sea level). The uncertainties are discussed in the text.

Table 5. Measured Kinematic Viscosities (ν/mm²·s⁻¹) for 1,3,5-Triisopropylcyclohexane (Mixture of e,e,e- and e,e,a Isomers) at Approximately 83 kPa (1650 m above Sea Level)[a]

T/°C	ν/mm²·s⁻¹	$U(\nu)$/mm²·s⁻¹
20.00	7.660	(0.014)
25.00	6.268	(0.009)
30.00	5.225	(0.009)
35.00	4.432	(0.010)
40.00	3.810	(0.011)
45.00	3.322	(0.011)
50.00	2.903	(0.004)
55.00	2.582	(0.004)
60.00	2.316	(0.004)
65.00	2.092	(0.003)
70.00	1.901	(0.003)
75.00	1.740	(0.004)
80.00	1.599	(0.003)
85.00	1.477	(0.003)
90.00	1.371	(0.003)
95.00	1.276	(0.003)
100.00	1.194	(0.004)

[a]The expanded uncertainties with a coverage factor k = 2 are provided parenthetically. Note that these measurements are for the equilibrium mixture of the two geometrical isomers.

mentioned in the Experimental Section) are observed for both the e,e,e and the e,e,a-geometrical isomers. This confirms the structural assignment, and it demonstrates that the NMR method is giving quantitative integrals with acceptable uncertainty for carbon-peak assignment. In this case (for the data in Table 1), what we mean by acceptable uncertainty is simply the ability to unambiguously distinguish between carbon atoms.

A comparison of peak areas allows the relative abundance of each isomer to be calculated. For the e,e,e-geometry isomer, only the peak at 44.18 ppm (representing three carbons in the e,e,e-geometry isomer with a relative area of 3.000) is baseline-resolved from the other peaks, so it was used for the calculation.
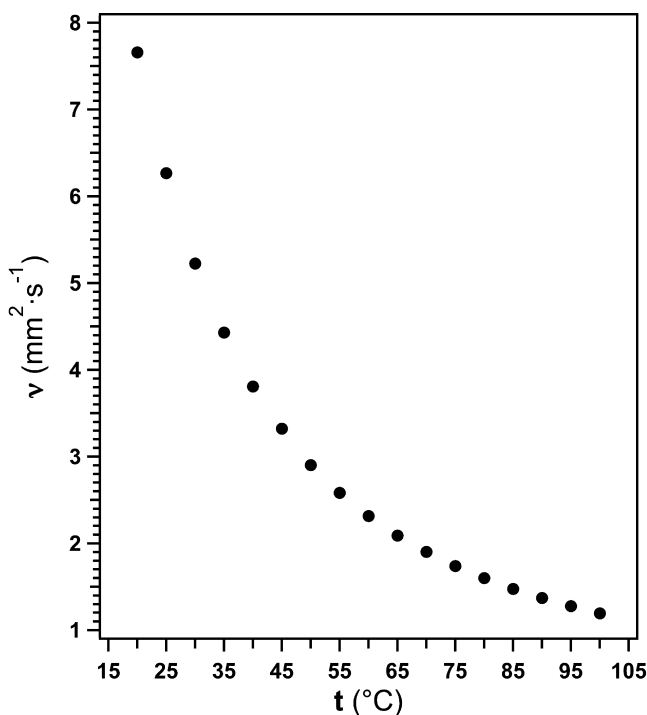
There are several baseline-resolved peaks for the e,e,a-geometry isomer, and all of these were added together and used for the calculation: 41.39 ppm, 38.34 ppm, 34.09 ppm, 31.94 ppm, 26.79 ppm, and 21.62 ppm (representing nine carbons in the e,e,a-geometry isomer with a total relative area of 1.093). These peak areas show that the sample of 1,3,5-triisopropylcyclohexane is 11 % e,e,a-isomer and 89 % e,e,e-geometry isomer. These percentages are remarkably close to the relative areas of the raw uncalibrated peaks obtained by GC-MS. The reason for this good agreement is very likely that the mass spectrometer has nearly equal sensitivity to both isomers; the chromatographic response factors are very similar. As a final note, it is no surprise that the e,e,e-geometry isomer predominates, because this isomer has a conformation with all of the bulky isopropyl groups in the energetically favored equatorial positions of the

Figure 6. Kinematic viscosity (ν/mm$^2 \cdot$s^{-1}) as a function of temperature for 1,3,5-triisopropylcyclohexane at approximately 83 kPa (1650 m above sea level). The uncertainties are discussed in the text.

cyclohexane ring. On the other hand, the e,e,a-geometry isomer always has at least one isopropyl group in a less favored axial position.

As stated earlier, we also applied ^{1}H NMR spectroscopy on the sample of 1,3,5-triisopropylcyclohexane. The spectrum was unremarkable in that the expected multiplets were observed for the aliphatic protons. Extensive peak overlap hampers the type of simple structural analysis that is possible with quantitative ^{13}C NMR. Because this spectrum is less informative than the ^{13}C spectrum, it will not be discussed further.

Kovats' Retention Index. The isothermal Kovats' retention index of 1,3,5-triisopropylcyclohexane was calculated by use of GC-MS with the following defining equation:

$$I_{sample}(T) = 100 \left[\frac{\log X_S - \log X_L}{\log X_H - \log X_S} + n_L \right] \qquad (1)$$

Here, I_{sample} is the dimensionless Kovats' retention index that is a function n of both temperature and the stationary phase employed. We used 5 % phenyl-95 %-dimethyl polysiloxane. The terms represented by X are retention parameters of the sample and standards. Any retention parameter, such as the adjusted retention time, t/min, the net retention volume, V_N/mL, the adjusted net retention volume, V_N^0, and the relative retentions, $r_{a/b}$, can be used. X_S is the retention parameter of the sample under consideration, X_L is the retention parameter of a normal alkane (that is straight chain or unbranched) of carbon number n_L that elutes earlier than the sample, and X_H is the retention parameter of a normal alkane having a carbon number greater than $n_L + 1$ that elutes after the sample.

The Kovats' retention index was determined with t' for 1,3,5-triisopropylcyclohexane at 150 °C, 175 °C, 200 °C, and 225 °C by use of n-alkanes with carbon numbers 7 to 18. Table 2a,b

presents the measurements for the e,e,e-1,3,5-triisopropylcyclohexane and e,e,a-1,3,5-triisopropylcyclohexane, respectively, as a function of temperature. The combined experimental uncertainties with a coverage factor (k = 2) are provided parenthetically.

The Kovats' retention index is significant in that it represents the coelution of a sample with a hypothetical n-alkane with a carbon number of I/100. Thus, at 150 °C on 5 % phenyl-95 %-dimethyl polysiloxane, e,e,e-1,3,5-triisopropylcyclohexane will coelute with a hypothetical n-alkane of 13.76 carbon atoms. While this may at first glance seem fictitious, it is nevertheless of great value in the prediction and description of intermolecular interactions.[20,21]

The temperature dependence of I_{sample} is known to follow a hyperbolic form similar to the familiar Antoine equation used to represent vapor pressure:[22]

$$I_{sample}(T) = A + \frac{B}{(T + C)} \qquad (2)$$

In this equation, A, B, and C are empirically determined constants, and T is the temperature (in °C). A nonlinear fitting routine was used to determine these constants. When retention indices are available for at least three temperatures, initial values for A, B, and C can be determined by use of the following eqs 3 to 5.

$$C = \frac{(T_2 - T_1)(I_3 T_3 - I_1 T_1) + (T_3 - T_1)(I_1 T_1 - I_2 T_2)}{(T_3 - T_1)(I_2 - I_1) - (T_2 - T_1)(I_3 - I_1)} \qquad (3)$$

$$A = \frac{I_2 T_2 - I_1 T_1 + C(I_2 - I_1)}{T_2 - T_1} \qquad (4)$$

$$B = (I_2 - A)(T_2 + C) \qquad (5)$$

In these eqs, I_1/min, I_2/min, and I_3/min are retention indices of the sample measured at temperatures T_1/K, T_2/K, and T_3/K. When additional retention indices are available at other temperatures, we advocate the use of minimum deviation estimates from eqs 3 to 5 to furnish the starting values for the nonlinear fit. When retention indices at four temperatures are available (such as in this work, for example), the best starting values are obtained from the I_1, I_2, and I_3 triplet that minimizes the deviation with the experimental value of I_4 with that produced by eq 2. Thus, four sets of A, B, and C are calculated, and the set producing the smallest deviation in I_4/min is chosen for the starting values for the nonlinear fit. This approach provides the fastest convergence, and also helps avoid converging to local minima. By use of this procedure, we determined the coefficients which are provided along with the measured indices in Table 2a,b. The deviation of the predicted retention indices with the measured indices is given as the mean squared error. Predictions made by use of eq 2 can be used for retention indices within the measured temperature range as well as extrapolation somewhat beyond that range on a case by case basis.

It is also of value to report the temperature dependence as a slope coefficient, δI_{sample}/10 °C, the variation of I_{sample} for a particular stationary phase over a particular temperature range. While not as reliable as the Antoine type fit, this coefficient is useful for predictions within the range of the measured results. These coefficients are also provided in Table 2a,b.

Boiling Temperature−Vapor Pressure. To obtain a single vapor pressure point as an anchor for equation of state

parameters, we measured the boiling temperature of 1,3,5-triisopropylcyclohexane at ambient atmospheric pressure. This was done in an apparatus used for the Advanced Distillation Curve (ADC) measurement.[23−25] The method and apparatus for the distillation curve measurement have been reviewed in a number of sources, so an additional general description will not be provided here. The required volume of fluid for the measurement (in this case 10 mL) was placed into a 50 mL boiling flask, which was itself placed into an aluminum enclosure equipped with cartridge heaters. A distillation head was then placed on the flask, with provision for temperature measurement. Calibrated, thermally tempered thermocouples were then inserted into the proper locations to monitor $T_k/°C$, the temperature in the fluid, and T_h, the temperature at the bottom of the takeoff position in the distillation head. Enclosure heating was then commenced with a variable transformer. In the typical ADC measurement on a complex mixture, a temperature difference of approximately 20 degrees between $T_k/°C$ and $T_h/°C$ is observed. When a pure fluid[26] or an azeotrope[27] is measured, this difference becomes very small and thus allows the measurement of a precise boiling temperature. We measured a boiling temperature of 240.3 °C, with an uncertainty of 0.2 °C, at an ambient atmospheric pressure of 83.071 kPa (the location of the laboratory in which the measurements reported herein were performed is approximately 1650 m above sea level), with an expanded uncertainty of 0.005 kPa. We do not apply any adjustment for sea level atmospheric pressure. This temperature might strictly be described as an initial boiling temperature of the binary mixture of e,e,e-geometry and e,e,a-geometry isomers.

We note that after the measurement, which took approximately 5 min at temperature, a slight yellow cast appeared in the sample of 1,3,5-triisopropylcyclohexane after it was recovered from the boiling flask. This coloration was not noted during the measurement. There was no apparent change in odor in the recovered fluid. No analysis was applied to this liquid. More complete consideration of the reaction products and decomposition kinetics will be presented separately.

Refractive Index. The refractive index of a fluid is a very useful parameter for identification, purity assessment, and in the modeling of solvatochromic parameters.[28,29] The refractive index of 1,3,5-triisopropylcyclohexane (binary mixture of geometrical isomers) was measured with an Abbe type refractometer, thermostatted with a circulating liquid bath, measuring with the sodium D line at 589 nm. The refractometer was calibrated at 20 °C with a standard glass block (refractive index = 1.52206, with 1-bromonaphthalene as the contact fluid), and the calibration was verified with the measurement of the refractive indices of distilled water and carbon disulfide. The refractive indices for 1,3,5-triisopropylcyclohexane are provided in Table 3.

Density, Speed of Sound, and Kinematic Viscosity. The density $(\rho/\text{kg}\cdot\text{m}^{-3})$, speed of sound $(w/\text{m}\cdot\text{s}^{-1})$, and kinematic viscosity $(\nu/\text{T}\cdot\text{Pa}^{-1})$ of 1,3,5-triisopropylcyclohexane (binary mixture of geometrical isomers) were measured at ambient atmospheric pressure (approximately 83 kPa in Boulder, CO). For all measurements, the sample liquid was used as it was received.

A commercial density and sound speed analyzer was used to simultaneously measure both properties from 5 to 70 °C. The instrument contains two measurement cells in series, a sound speed cell that measures the propagation time of ~3 MHz sound waves, and a vibrating tube densimeter constructed of borosilicate glass. Both cells are housed in a thermostatted copper block, the temperature of which is controlled with a combination of thermoelectric Peltier elements and an integrated Pt-100 resistance thermometer. The instrument was calibrated with deionized water, toluene, and isooctane. During measurements, temperature scans were performed from (70 to 5) °C in decrements of 5 °C. A fresh aliquot of sample was injected prior to the start of each temperature scan, and a total of five scans were performed in this work. Additional details about the density and sound speed analyzer can be found elsewhere.[30,31]

A commercial automated open gravitational glass capillary viscometer was used to measure kinematic viscosity from (20 to 100) °C. The viscometer consists of a suspended-level Ubbelohde glass capillary, two timing bulbs with a combined measurement range of approximately 0.3 mm²·s⁻¹ to 30 mm²·s⁻¹, and three thermistor sensors that detect the passing of the sample liquid meniscus. The viscometer is immersed in a thermostatted bath filled with silicone oil, the temperature of which is controlled with a combination of a stirrer, thermo-electric Peltier elements, and an internal Pt-100 resistance thermometer. An external platinum resistance thermometer is also suspended in the bath for use as a temperature reference. The instrument was calibrated with certified viscosity standards. During measurements, a single sample aliquot of approximately 15 mL was measured in a programmed scan from (20 to 100) °C in 5 °C increments. At each temperature, efflux time measurements were repeated until three consecutive tests agreed within 0.25 %. Additional details about the open gravitational capillary viscometer can be found elsewhere.[30]

Measurement results from the density and sound speed analyzer are shown in Table 4 and Figure 5. Reported values are averaged results for five temperature scans. Also included in Table 4 and Figure 5 are adiabatic compressibilities (κ_s), which were calculated from measured quantities via the relation:

$$\kappa_s = \frac{1}{\rho \cdot w^2} \qquad (6)$$

where ρ is density, w is speed of sound, and the subscript s indicates "at constant entropy".

The kinematic viscosity data are shown in Table 5 and Figure 6. Reported values are averaged results for the first three consecutive measurements that met the specified acceptance criterion (maximum spread ≤ 0.25 %).

■ CONCLUSION

In this paper, we have provided some basic chemical and thermophysical measurement data on 1,3,5-triisopropylcyclohexane, a fluid that is being considered for inclusion in a surrogate mixture palette for diesel fuel. This fluid is important because it provides a unique and critical ingredient for a diesel fuel surrogate: a multiply substituted, low cetane number, high molecular mass monocycloalkane. The measurements are significant in that this fluid is not commercially available, and to our knowledge, no measurements on this fluid have been previously published. They are also significant in that we take explicit account of the two geometrical isomers (e,e,e and e,e,a) that are present at equilibrium for this fluid, and where possible, we report measurements that are specific to those individual isomers.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: bruno@boulder.nist.gov; tel.: 303-497-5158; fax: 303-497-5044.

■ REFERENCES

(1) Tsang, W.; Hudgens, J.; Allison, T. C.; Burgess, D. R.; Manion, J. A.; Matheu, D. *Workshop on combustion simulation databases for real transportation fuels*, Workshop Report, NIST-IR 7155, National Institute of Standards and Technology, Gaithersburg, MD, September 4−5, 2003.

(2) Colket, M.; Edwards, T.; Williams, S.; Ceranasky, N. P.; Miller, D.; Egolfopolous, F.; Linstedt, P.; Deshadri, K.; Dryer, F. L.; Law, C. K.; Friend, D.; Lenhert, D. B.; Pitch, H.; Sarofin, A.; Smooke, M.; Tsang, W. *Development of an experimental database and kinetic models for surrogate jet fuels*. http://www.stanford.edu/group/pitsch/publication/ColketJet_Fuel_Surrogate_AIAA_2007.pdf (accessed May 2012).

(3) Colket, M.; Edwards, J. T.; Williams, S.; Cernansky, N. P.; Miller, D. L.; Egolfopoulos, F.; Dryer, F. L.; Bellan, J.; Linstedt, P.; Seshadri, K.; Pitch, H.; Sarofim, A. *Identification of target validation data for development of surrogate jet fuels*, AIAA Paper 2008-972, 46th AIAA Aerospace Sciences Meeting and Exhibit, Reno, NV, January 7−10, 2008; American Institute of Aeronautics and Astronautics.

(4) Multi-Agency Coordinating Committee on Combustion Research (MACCCR). http://www.nsf.gov/eng/cbet/macccr (accessed May 2012).

(5) Andersen, V. F.; Anderson, J. E.; Wallington, T. J.; Mueller, S. A.; Nielsen, O. J. Distillation curves for alcohol gasoline blends. *Energy Fuels* 2010, 24 (4), 2683−2691.

(6) Huber, M. L.; Smith, B. L.; Ott, L. S.; Bruno, T. J. Surrogate Mixture Model for the Thermophysical Properties of Synthetic Aviation Fuel S-8: Explicit Application of the Advanced Distillation Curve. *Energy Fuels* 2008, 22, 1104−1114.

(7) Huber, M. L.; Lemmon, E. W.; Diky, V.; Smith, B. L.; Bruno, T. J. Chemically authentic surrogate mixture model for the thermophysical properties of a coal-derived-liquid fuel. *Energy Fuels* 2008, 22, 3249−3257.

(8) Huber, M. L.; Lemmon, E.; Kazakov, A.; Ott, L. S.; Bruno, T. J. Model for the thermodynamic properties of a biodiesel fuel. *Energy Fuels* 2009, 23, 3790−3797.

(9) Huber, M. L.; Lemmon, E.; Ott, L. S.; Bruno, T. J. Preliminary surrogate mixture models for rocket propellants RP-1 and RP-2. *Energy Fuels* 2009, 23, 3083−3088.

(10) Huber, M. L.; Lemmon, E. W.; Bruno, T. J. Surrogate mixture models for the thermophysical properties of aviation fuel Jet-A. *Energy Fuels* 2010, 24, 3565−3571.

(11) Bruno, T. J.; Smith, B. L. Evaluation of the physicochemical authenticity of aviation kerosene surrogate mixtures Part I: Analysis of volatility with the advanced distillation curve. *Energy Fuels* 2010, 24, 4266−4276.

(12) Bruno, T. J.; Huber, M. L. Evaluation of the physicochemical authenticity of aviation kerosene surrogate mixtures Part II: Analysis

and prediction of thermophysical properties. *Energy Fuels* 2010, 24, 4277−4284.

(13) Mueller, C. J.; Cannella, W. J.; Bruno, T. J.; Bunting, B.; Dettman, H. D.; Franz, J. A.; Huber, M. L.; Natarajan, M.; Pitz, W. J.; Ratcliff, M. A.; Wright, K. Methodology for formulating diesel surrogate fuels with accurate compositional, ignition-quality, and volatility characteristics. *Energy Fuels* 2011, in press.

(14) Mendenhall, G. D. Personal communication. Eastern Sources, Elmsford, NY, November 2010.

(15) http://www.easternsourcess.com (accessed May 2012).

(16) Radcliff, M. Personal communication (derived cetane number of 1,3,5-triisopropylcyclohexane). National Renewable Energy Laboratory, Golden, CO, 2011.

(17) Bruno, T. J., Svoronos, P. D. N. *CRC Handbook of Fundamental Spectroscopic Correlation Charts*; Taylor and Francis CRC Press: Boca Raton, 2006.

(18) Bruno, T. J., Svoronos, P. D. N. *CRC Handbook of Basic Tables for Chemical Analysis*, 3rd ed; Taylor and Francis CRC Press: Boca Raton, 2011.

(19) Schoolery, J. N. Some quantitative applications of ^{13}C NMR spectroscopy. *Prog. Nucl. Magn. Reson. Spectrom.* 1997, 11, 79−93.

(20) Lagalante, A. F.; Hall, R. L.; Bruno, T. J. Kamlet-Taft solvatochromic parameters of the sub- and supercritical fluorinated ethane solvents. *J. Phys. Chem. B* 1998, 102, 6601−6604.

(21) Lagalante, A. F.; Wood, C.; Clarke, A. M.; Bruno, T. J. Kamlet-Taft solvatochromic parameters for 25 glycol ether solvents and glycol ether aqueous solutions. *J. Solution Chem.* 1998, 27 (10), 887−900.

(22) Bruno, T. J.; Wertz, K. H.; Cacairi, M. Kovats retention indices of halocarbons on a hexafluoropropylene epoxide-modified graphitized carbon black. *Anal. Chem.* 1996, 68, 1347−1359.

(23) Bruno, T. J.; Ott, L. S.; Smith, B. L.; Lovestead, T. M. Complex fluid analysis with the advanced distillation curve approach. *Anal. Chem.* 2010, 82, 777−783.

(24) Bruno, T. J.; Ott, L. S.; Lovestead, T. M.; Huber, M. L. The composition explicit distillation curve technique: relating chemical analysis and physical properties of complex fluids. *J. Chromatogr.* 2010, A1217, 2703−2715.

(25) Bruno, T. J.; Ott, L. S.; Lovestead, T. M.; Huber, M. L. Relating complex fluid composition and thermophysical properties with the advanced distillation curve approach. *Chem. Eng. Technol.* 2010, 33 (3), 363−376.

(26) Bruno, T. J., Huber, M. L., Laesecke, A, Lemmon, E. W., Perkins, R. A. *Thermochemical and thermophysical properties of JP-10*, NIST-IR 6640; National Institute of Standards and Technology: Gaithersburg, MD, 2006.

(27) Hadler, A. B.; Ott, L. S.; Bruno, T. J. Study of azeotropic mixtures with the advanced distillation curve approach. *Fluid Phase Equilib.* 2009, 281, 49−59.

(28) Lagalante, A. F.; Bruno, T. J. Modeling the Water-Supercritical CO_2 Partition Coefficients of Organic Solutes Using a Linear Solvation Energy Relationship. *J. Phys. Chem. B* 1998, 102, 907−909.

(29) Lagalante, A. F.; Clarke, A. M.; Bruno, T. J. Modeling the Water-R134a Partition Coefficients of Organic Solutes Using a Linear Solvation Energy Relationship. *J. Phys. Chem. B* 1998, 102, 8889−8892.

(30) Laesecke, A.; Fortin, T. J.; Splet, J. D. Density, speed of sound, and viscosity measurements of reference materials for biofuels. *Energy Fuels* 2012, 26, 1844−1861.

(31) Fortin, T. J.; Laesecke, A.; Freund, M.; Outcalt, S. L. Advanced calibration, adjustment, and operation of a density and sound speed analyzer. *J. Chem. Thermodyn.*, submitted.