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Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for 1,4-Diisopropylbenzene, 1,2,4,5-Tetraisopropylbenzene, Cyclohexanone Oxime, Dimethyl Malonate, Glutaric Acid, and Pimelic Acid

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The results of a study aimed at improvement of group-contribution methodology for estimation of enthalpies of formation in the ideal-gas state for pure organic substances are reported. Specific weaknesses where particular group-contribution terms were unknown, or estimated because of lack of experimental data, are addressed by experimental studies of enthalpies of combustion in the condensed phase, vapor-pressure measurements, and differential scanning calorimetric (DSC) heat-capacity measurements. Enthalpies of formation in the condensed phase were determined for 1,4-diisopropylbenzene, 1,2,4,5-tetraisopropylbenzene, dimethyl malonate, glutaric acid, pimelic acid, and cyclohexanone oxime. Ideal-gas enthalpies of formation for each of the compounds except pimelic acid are also reported. Enthalpies of fusion and for crystalline phase transitions were determined for 1,2,4,5-tetraisopropylbenzene, cyclohexanone oxime, glutaric acid, and pimelic acid. Two-phase (solid + vapor) or (liquid + vapor) heat capacities were determined from 300 K to the critical region or earlier decomposition temperature for all the title compounds. For 1,4-diisopropylbenzene, 1,2,4,5-tetraisopropylbenzene, and dimethyl malonate, values of the critical temperature and critical density were determined from the DSC results and the corresponding critical pressure was derived from the fitting procedures. The results of all the measurements were combined to derive a series of thermophysical properties including critical temperature, critical density, critical pressure, acentric factor, enthalpies of vaporization (restricted to within ±50 K of the temperature range of the vapor pressures), and heat capacities along the saturation line. Wagner-type vapor-pressure equations were derived for each compound. Enthalpies of sublimation were derived for cyclohexanone oxime and, using literature vapor pressures, glutaric acid. Group-additivity enthalpy of formation parameters and strain energies useful in the application of ideal-gas-phase group-contribution correlations were derived. Errors in the literature data for the enthalpy of formation of diethyl malonate are noted.

Introduction

This research was funded jointly by the U.S. Department of Energy (DOE), through the Office of Fossil Energy within the Processing and Downstream Operations section of the Advanced Oil Recovery (AOR) program, and the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers, through some of its member industrial organizations. The objective of this ongoing project is to expand the group-additivity method of calculation of gas-phase thermodynamic properties by determining thermochemical data on compounds containing unique groups or atomic environments. The work performed in the 11th year of this project (DIPPR Research Project 871: Determination of Pure Compound Ideal-Gas Enthalpies of Formation) represents the outcome of a meeting in late 1996, and subsequent communications, in which representatives of the DOE National Petroleum Technology Office, DIPPR, and BDM Oklahoma at the National Institute for Petroleum and Energy Research (NIPER) agreed on a list of compounds for which the determination of the enthalpy of formation in the ideal-gas state would be of benefit to all the participants.

Six compounds were chosen for experimental studies. The molecular structures, Chemical Abstract Service (CAS) names, commonly used trivial names, and CAS Registry Numbers of the compounds studied are listed in Figure 1. Of the six compounds studied, only two (1,4-diisopropylbenzene and dimethyl malonate) were liquids at ambient temperature. The derivation of ideal-gas standard enthalpies of formation for each of the compounds required experimental measurements in addition to the determination of the standard enthalpies of combustion. A listing of the auxiliary measurements made for each of the compounds is given in Table 1. In addition, when the research started, it was hoped that weight-loss effusion vapor pressure measurements using a Knudsen-type effusion apparatus[1−3] would be used to determine vapor pressures in the vicinity of 298.15 K (and hence via the Clausius−Clapeyron equation the standard enthalpy of sublimation) for both glutaric and pimelic acid. However, “The best laid schemes o, mice an’ men Gang aft a-gley”.[4] The effusion apparatus was never completely functional in time for completion of the measurements.

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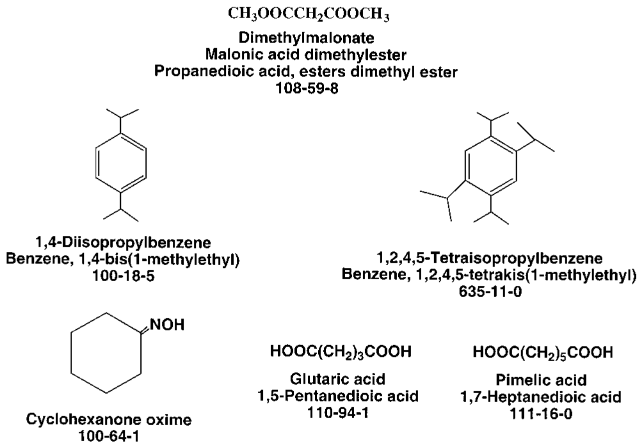


Figure 1. Structural formulas, common names, Chemical Abstracts Service names (provided by the authors), and Chemical Abstracts Service Registry Numbers (provided by the authors) for the compounds studied in this research.

Table 1. Outline of the Measurements Performed in This Project[a]

compd (state)	$\Delta_c U^\circ_m$	vapor pressure	heat capacity	T_c, ρ_c[b]
1,4-diisopropylbenzene	x	x	x	x
1,2,4,5-tetraisopropylbenzene	x	x	x	x
dimethyl malonate	x	x	x	x
glutaric acid	x		x	
pimelic acid	x		x	
cyclohexanone oxime	x	x	x	

[a] Measurements made are denoted by x. [b] From DSC measurements (a value for the critical pressure was derived using the fitting procedures).

The purity of the sample employed in a measurement of a thermodynamic property can significantly affect the accuracy of the measurement. The degree of inaccuracy introduced by the presence of impurities depends on a number of factors. In the case of the measurement of energies of combustion, with CO_2 analyses determining the amount of reaction, nonisomeric impurities are highlighted. The presence of a small amount of water (say 0.05 mol %) in the sample will often not be detected in the gas–liquid chromatographic analysis of the sample but will be indicated by a low CO_2 recovery. Then the determination of the energy of combustion should be based on the CO_2 analysis and not the mass of sample used in the calorimetric measurement. The presence of small amounts (less than 0.1%) of isomeric impurities usually will not have a significant effect on the result. However, this rule of thumb must be used with care, especially if the major impurity is an isomer with increased stability due to resonance or instability due to steric interactions. Measurements on samples whose purities are >99.95 mol % is a goal of this project.

There are in the literature numerous sets of Benson group parameters for the estimation of enthalpies of formation for pure organic materials: Benson,[5] Benson et al.,[6] Cox and Pilcher,[7] Benson,[8] Reid et al.,[9] Cohen and Benson,[10] Domalski and Hearing,[11] and Cohen,[12] to name just a few. In addition, there are various other schemes that use extensions of the methodology, for example, Pedley et al.[13] and Pedley.[14] Also, in several papers, for example, Eigenmann et al.,[15] corrections to earlier work (in that case Benson[5]) were made. All these sets of parameters are different and cannot be interlaced. For example, the group C−(C)$_3$(H) has a value of −7.95 kJ (−1.90 kcal) in ref 8. In ref 9 the corresponding value is also −7.95 kJ, but it is listed as −1.17 kJ in ref 11 and as −10.0 kJ in ref 12. To complicate the picture even more, it is believed that Reid et al.[9] used a value of 4.1868 and not 4.184 to convert from the thermochemical calorie used by Benson in his 1976 text[8] to the values reported in their text. By missing the Eigenmann et al. (1973) reference,[15] Reid et al.[9] did, inadvertently, use a mixture of corrected and outdated values for various oxygen-containing groups.

The differing sets of Benson group parameters need to be drawn together in one new comprehensive text. The articles by Cohen and Benson (1993)[10] and Cohen (1996)[12] represent partial attempts at that, but they are not nearly as comprehensive as the early work by Benson. Until someone or some group undertakes and completes the task, care should be taken in the selection of consistent sets of parameters. In the work reported on this project, care is taken to list *exactly* what group parameters are used in the additivity calculations, for example, the C−(C)$_3$(H) group has a value of −7.95 kJ in all the calculations performed within the project. An attempt is made to use only Reid et al.[9] values, falling back on the Benson 1976 tables[8] if necessary and specially noting any and all exceptions. By doing this, reference is made to the most probable set of tables used by a practicing chemical engineer, and any errors in that text are highlighted.

Experimental Section

Since the combustion calorimetric techniques used differ from compound to compound, details of the combustion calorimetric methodology are given below. The apparatus and procedures used in obtaining the auxiliary experimental data (see Table 1) necessary to derive the ideal-gas enthalpies of formation have been previously described in the literature and in various DOE reports. In addition, the earlier papers published in this Journal under the DIPPR auspices[16−22] give detailed references to the experimental techniques and fitting procedures. Therefore, in this paper, little experimental detail are given and the reader is referred to refs 16−22 and the earlier publications referenced therein.

Materials. To minimize errors due to impurities, care was taken to ensure only samples of high purity (>99.9 mol % purity) were subjected to the thermophysical property measurements. All compounds were purchased from Aldrich Chemical Co. Gas liquid chromatographic (GLC) analyses on the purchased samples gave an average purity of 98 mol %, in agreement with Aldrich specifications. The samples of 1,4-diisopropylbenzene and dimethyl malonate were purified by repeated spinning-band distillations. Each of 1,2,4,5-tetraisopropylbenzene (200 passes), cyclohexanone oxime (150 passes), glutaric acid (175 passes), and pimelic acid (150 passes) was purified in a zone refiner. GLC analyses of the samples used in the measurements gave purities of at least 99.95 mol % for each compound. The high purity of each sample was confirmed subsequently by the percentage CO_2 recoveries in the combustion calorimetric measurements and/or by the small differences between the boiling and condensation temperatures in the ebulliometric vapor-pressure measurements listed in column 6 of Table 7. Cyclohexanone oxime proved to be an exception. Although the GLC analyses of samples of that compound resulted in purity determinations of >99.95 mol %, the subsequent percentage CO_2 recoveries represented a purity of 99.8 mol %. The remaining 0.2 mol % was assumed to be water.

All transfers of the purified samples were done under nitrogen or helium or by vacuum distillation. The water used as a reference material in the ebulliometric vapor-pressure measurements was deionized and distilled from potassium permanganate. The decane used as a reference material for the ebulliometric measurements was purified by urea complexation, two recrystallizations of the complex, decomposition of the complex with water, extraction with ether, drying with $MgSO_4$, and distillation at 337 K and 1 kPa pressure. GLC analysis of the decane sample failed to show any impurity peaks.

Physical Constants. Molar values are reported in terms of the 1991 relative atomic masses[23] and the gas constant, $R = 8.314\,51\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, adopted by CODATA.[24] The platinum resistance thermometers and the quartz crystal thermometer used in these measurements were calibrated by comparison with standard platinum resistance thermometers whose constants were determined at the National Institute of Standards and Technology (NIST) on IPTS-68. All temperatures were measured in terms of IPTS-68 and converted to ITS-90 with increments provided in the literature.[25,26] Measurements of mass, time, electric resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

Energy of Combustion Apparatus and Procedures. The apparatus and experimental procedures used in the combustion calorimetry of organic C, H, N, O compounds at the research facilities in Bartlesville, OK, have been described previously in refs 27−30.

A rotating-bomb calorimeter (laboratory designation BMR II)[31] and a platinum-lined bomb (laboratory designation Pt-3b)[32] with an internal volume of $0.3934\ \mathrm{dm^3}$ were used without rotation in the combustion calorimetric series. Flexible borosilicate-glass ampules[28,33] were used to confine the samples that were liquid at 298 K (1,4-diisopropylbenzene and dimethyl malonate). Cyclohexanone oxime, glutaric acid, and pimelic acid were burned as pellets enclosed in a polyester-film bag.[31] All experiments, after the first which defined the energy of combustion of the compound, were completed within 0.01 K of $T = 298.15$ K.

NIST thermochemical benzoic acid (sample 39i) was used for calibration of the calorimeter; its specific energy of combustion is $-(26\,434.0 \pm 3.0)\ \mathrm{J\cdot g^{-1}}$ under certificate conditions. Conversion to standard states[34] gives $-(26\,413.7 \pm 3.0)\ \mathrm{J\cdot g^{-1}}$ for $\Delta_c U^\circ_m/M$, the standard specific energy of the idealized combustion reaction. The combustion measurements were performed in two separate series five-months apart as the purified compounds became available. The first series of combustion measurements were made on just dimethyl malonate with interspersed calibrations. The temperature rise during those measurements was ∼1.4 K, somewhat less than the usual 2 K because of the low energy of combustion of the diester and the restricted ampule size because of the dimensions of the crucible. Nitrogen oxides were not formed in the calibration experiments or during the combustion calorimetry of any of the C, H, O compounds because of the high purity of the oxygen used and preliminary bomb flushing. The energy equivalent of the calorimeter, ϵ(calor), obtained during the dimethyl malonate combustion series was $(16\,773.1 \pm 0.3)\ \mathrm{J\cdot K^{-1}}$ (mean and standard deviation of six measurements). For the second series the energy equivalent of the calorimeter, ϵ(calor), was $(16\,774.3 \pm 0.5)\ \mathrm{J\cdot K^{-1}}$ (mean and standard deviation of six measurements).

Table 2. Physical Properties at 298.15 K[a]

compd (state)	ρ $\mathrm{kg\cdot m^{-3}}$	$10^7(\partial V/\partial T)_p$ $\mathrm{m^3\cdot K^{-1}}$	C_p/R
1,4-diisopropylbenzene (l)	852.5	(1.5)	35.4
1,2,4,5-tetraisopropylbenzene (cr)	1000	(0.3)	50.7
dimethyl malonate (l)	1150	(1.5)	18.1
glutaric acid (cr)	1425	(0.3)	20.6
pimelic acid (cr)	1290	(0.3)	23.0
cyclohexanone oxime (cr)	1100	(0.3)	22.3

[a] Values in parentheses are estimates. Values of density were measured, either from measurements of the volumes of the ampules used in the combustion calorimetry, and their enclosed sample masses, for the liquid samples (1,4-diisopropylbenzene and dimethyl malonate) or from the dimensions of a pellet of known mass for the remaining compounds that were solids at 298.15 K. Values of the heat capacity of each sample at 298.15 K were measured using DSC measurements.

Table 3. Carbon Dioxide Recoveries

compd	no. of expts	% recovery[a]
benzoic acid calibration	6	99.989 ± 0.004
dimethyl malonate	6	99.940 ± 0.007
benzoic acid calibration	6	99.982 ± 0.003
1,4-diisopropylbenzene	6	99.966 ± 0.004
1,2,4,5-tetraisopropylbenzene	6	99.900 ± 0.006[b]
glutaric acid	6	99.926 ± 0.006
pimelic acid	6	99.942 ± 0.006
cyclohexanone oxime	6	99.80 ± 0.02[c]

[a] Mean and standard deviation of the mean. [b] Glass present in sample (????). [c] Sample contained water.

The auxiliary oil (laboratory designation TKL66) had the empirical formula $CH_{1.913}$. For this material, $\Delta_c U^\circ_m/M$ was -$(46\,042.5 \pm 1.8)\ \mathrm{J\cdot g^{-1}}$ (mean and standard deviation). For the cotton fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta_c U^\circ_m/M$ was $-16\,945\ \mathrm{J\cdot g^{-1}}$. The value for $\Delta_c U^\circ_m/M$ obtained for the polyester film, empirical formula $C_{10}H_8O_4$, was a function of the relative humidity (RH) in the laboratory during the weighing.[31]

$$\{(\Delta_c U^\circ_m/M)/(\mathrm{J\cdot g^{-1}})\} = -22\,912.0 - 1.0560(\mathrm{RH}) \quad (1)$$

Information necessary for reducing the apparent mass measured in air to mass, for converting the energy of the actual bomb process to that of the isothermal process, and for reducing to standard states[34] is given in Table 2.

The values of density reported in Table 2 were measured in this laboratory, either from measurements of volumes of the ampules used in the combustion calorimetry, and their enclosed sample masses, for the liquid samples (1,4-diisopropylbenzene and dimethyl malonate) or from the dimensions of a pellet of known mass for the remaining compounds that were solids at 298.15 K. The values of the heat capacity of each sample at 298.15 K were measured during the differential scanning calorimetric measurements reported below.

Nitric acid, formed during combustion of the nitrogen-containing compound, cyclohexanone oxime, was determined by titration with standard sodium hydroxide.[35] Carbon dioxide was also recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as adsorbent for the CO_2 recoveries.[29] The combustion products were checked for unburned carbon and other products of incomplete combustion, but none was detected. Summaries of the carbon dioxide recoveries for each of the two calibration series and the corresponding compound energy determinations are listed in Table 3. As noted above, the sample of cyclohexanone oxime had water present and was analyzed on the basis of the CO_2 recoveries as 99.80 ± 0.02 mol % pure. All the reported values for energies and enthalpies of combustion are based on the mass of CO_2 recovered and not the sample mass combusted.

Table 4. Typical Combustion Experiments at 298.15 K for Each of the Compounds (p° = 101.325 kPa)[a,b]

	A	B	C	D	E	F
m'(compd)/g	0.717 729	0.721 222	1.207 894	1.926 997	1.452 725	0.940 731
m''(oil)/g	0.043 573		0.059 088			
m'''(mylar)/g		0.065 755		0.089 191	0.094 914	0.091 486
m''''(fuse)/g	0.002 249	0.002 690	0.002 990	0.002 691	0.002 904	0.030 89
$n_i(H_2O)$/mol	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35
m(Pt)/g	38.453	32.201	38.455	32.202	32.202	32.216
ΔT^c/K	2.006 61	2.019 71	1.425 33	1.994 58	1.996 40	2.001 79
ϵ(calor)(ΔT)/J	−33 655.0	−33 874.6	−23 907.1	−33 457.6	−33 488.1	−33 573.3
ϵ(cont)(ΔT)^d/J	−43.3	−40.1	−31.9	−42.7	−41.7	−40.3
ΔU_{ign}/J	0.8	0.8	0.8	0.8	0.8	0.8
ΔU(corr.std.states)/J^e	13.1	12.9	17.91	31.2	23.4	14.8
$\Delta U_{dec}(HNO_3)$/J						58.2
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	2006.2		2720.6			
$-m'''(\Delta_c U^\circ_m/M)$(mylar)/J		1501.4		2037.1	2167.2	2089.4
$-m''''(\Delta_c U^\circ_m/M)$(fuse)/J	38.1	45.6	50.7	45.6	49.2	52.3
$m'(\Delta_c U^\circ_m/M)$(compd)/J	−31 640.1	−32 354.0	−21 149.0	−31 385.6	−31 289.2	−31 398.1
$(\Delta_c U^\circ_m/M)$(compd)/J·g^{-1}	−44 083.7	−44 860.0	−17 509.1	−16 287.3	−21 538.3	−33 376.5

[a] **A** = 1,4-diisopropylbenzene; **B** = 1,2,4,5-tetraisopropylbenzene; **C** = dimethyl malonate; **D** = glutaric acid; **E** = pimelic acid; and **F** = cyclohexanone oxime. [b] The symbols and abbreviations of this table are those of ref 34 except as noted. [c] $\Delta T/\mathrm{K} = (T_i - T_f + \Delta T_{corr})/\mathrm{K}$. [d] $\epsilon_i(\mathrm{cont})(T_i - 298.15\ \mathrm{K}) + \epsilon_f(\mathrm{cont})(298.15\ \mathrm{K} - T_f + \Delta T_{corr})$. [e] Items 81 to 85, 87 to 90, 93, and 94 of the computational form of ref 34.

Table 5. Energy of Combustion Results (T = 298.15 K and p° = 101.325 kPa)[a,b]

compd	$\{(\Delta_c U^\circ_m/M)(\mathrm{compd})\}/(\mathrm{J \cdot g^{-1}})$	$\langle\{(\Delta_c U^\circ_m/M)(\mathrm{compd})\}/(\mathrm{J \cdot g^{-1}})\rangle$
1,4-diisopropylbenzene	−44 083.7, −44 078.0, −44 080.4, −44 084.9, −44 078.2, −44 083.5	−44 081.4 ± 1.2
1,2,4,5-tetraisopropylbenzene	−44 851.2, −44 860.0, −44 859.2, −44 860.6, −44 854.2, −44 860.0	−44 857.6 ± 1.6
dimethyl malonate	−17 509.1, −17 508.3, −17 512.1, −17 510.3, −17 504.3, −17 510.6	−17 510.1 ± 0.7
glutaric acid	−16 278.3, −16 290.9, −16 293.8, −16 283.6, −16 288.7, −16 288.7	−16 288.8 ± 1.4
pimelic acid	−21 538.3, −21 545.6, −21 539.7, −21 538.8, −21 540.5, −21 533.3	−21 539.4 ± 1.6
cyclohexanone oxime	−33 376.5, −33 370.9, −33 367.2, −33 367.2, −33 378.5, −33 371.5	−33 372.0 ± 1.9

[a] The uncertainties shown are one standard deviation of the mean. [b] All the energy of combustion measurements made for each compound are listed in this table.

Table 6. Condensed-Phase Molar Thermochemical Functions at 298.15 K and p° = 101.325 kPa[a]

compd (state)	$\Delta_c U^\circ_m$/kJ·mol^{-1}	$\Delta_c H^\circ_m$/kJ·mol^{-1}	$\Delta_f H^\circ_m$/kJ·mol^{-1}
1,4-diisopropylbenzene (l)	−7153.36 ± 1.04	−7164.52 ± 1.04	−130.07 ± 1.22
1,2,4,5-tetraisopropylbenzene (cr)	−11054.6 ± 1.7	−11073.2 ± 1.7	−297.4 ± 2.0
dimethyl malonate (l)	−2313.37 ± 0.32	−2313.37 ± 0.32	−797.50 ± 0.44
glutaric acid (cr)	−2152.03 ± 0.46	−2152.03 ± 0.46	−958.84 ± 0.54
pimelic acid (cr)	−3449.97 ± 0.68	−3452.45 ± 0.68	−1017.1 ± 0.8
cyclohexanone oxime (cr)	−3776.38 ± 0.68	−3780.41 ± 0.68	−152.41 ± 0.76

[a] The results listed in this table are for the stable [liquid (l) or crystalline (cr)] condensed phase at 298.15 K for each of the compounds.

Results

Combustion Calorimetry. A typical combustion experiment for each C, H, O, N compound studied is summarized in Table 4. It is impractical to list summaries for each combustion. $\Delta_c U^\circ_m/M$ values for all the combustion calorimetric measurements made on each of these compounds are reported in Table 5. The values of $\Delta_c U^\circ_m/M$ in Tables 4 and 5 for the C, H, O, N compounds refer to the general reaction

$$C_aH_bO_cN_d(\mathrm{cr\ or\ l}) + \left(a + \frac{b}{4} - \frac{c}{2}\right)O_2(g) = aCO_2(g) + \frac{b}{2}H_2O(l) + \frac{d}{2}N_2(g) \quad (2)$$

As noted above, all the values of $\Delta_c U^\circ_m/M$ refer to unit mass of sample derived from the corresponding carbon dioxide analyses of the combustion products. Corrections for the small amounts of nitric acid, formed during the combustions of the cyclohexanone oxime sample, were made during the conversion to standard states[34] based on a value of −59.7 kJ·mol^{-1} for the energy of formation of 0.1 mol·dm^{-3} HNO_3(aq) from N_2, O_2, and H_2O(l).

Table 6 gives derived values of the standard molar energy of combustion $\Delta_c U^\circ_m$; the standard molar enthalpy of combustion $\Delta_c H^\circ_m$; and the standard molar enthalpy of formation $\Delta_f H^\circ_m$ for the compounds studied. Values of $\Delta_c U^\circ_m$ and $\Delta_c H^\circ_m$ for the C, H, O, N compounds refer to eq 2. The corresponding values of $\Delta_f H^\circ_m$ refer to the reaction

$$aC(\mathrm{cr,\ graphite}) + \frac{b}{2}H_2(g) + \frac{c}{2}O_2(g) + \frac{d}{2}N_2(g) = C_aH_bO_cN_d(\mathrm{cr\ or\ l}) \quad (3)$$

The uncertainties given in Table 6 are the "uncertainty interval" as defined by Rossini.[36] The enthalpies of formation of CO_2(g) and H_2O(l) were taken to be −(393.51 ± 0.13) kJ·mol^{-1} and −(285.830 ± 0.042) kJ·mol^{-1}, respectively, as assigned by CODATA.[37]

Vapor-Pressure Measurements. Ebulliometric vapor pressure measurements were made on three compounds: 1,4-diisopropylbenzene, 1,2,4,5-tetraisopropylbenzene, and dimethyl malonate. The results of the measurements are reported in Table 7. In the table the vapor pressure, the condensation temperature, and the difference between the condensation and boiling temperatures are reported. The small differences between the boiling and condensation temperatures in the ebulliometric measurements indicated correct operation of the equipment and the high purity of the samples studied.

Table 7. Summary of Vapor-Pressure Results[a]

standard	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K	standard	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
1,4-Diisopropylbenzene											
decane	365.513	2.0135	0.0000	0.0003	0.040	water	453.487	47.357	0.000	0.005	−0.001
decane	380.970	4.0011	0.0000	0.0005	0.016	water	460.896	57.809	−0.002	0.006	−0.002
decane	387.932	5.3328	−0.0001	0.0006	0.012	water	468.335	70.089	0.001	0.006	−0.001
decane	398.295	7.9940	0.0002	0.0009	0.007	water	475.850	84.513	0.000	0.008	−0.001
decane	406.084	10.656	0.000	0.001	0.004	water	483.410	101.300	−0.003	0.009	−0.002
decane	412.384	13.315	0.000	0.001	0.003	water	491.019	120.76	0.00	0.01	−0.001
decane	418.959	16.653	0.000	0.002	0.002	water	498.681	143.19	0.00	0.01	−0.001
decane	424.411	19.917	0.000	0.002	0.000	water	506.394	168.95	0.00	0.01	0.000
water	431.651	25.046	0.001	0.003	0.000	water	514.171	198.44	0.00	0.01	0.000
water	438.864	31.178	0.000	0.003	0.000	water	521.983	231.94	0.00	0.02	0.000
water	446.148	38.556	−0.001	0.004	−0.001	water	529.860	269.98	−0.01	0.02	0.001
1,2,4,5-Tetraisopropylbenzene											
decane	409.874	2.0010	−0.0001	0.0003	0.020	water	502.379	47.382	0.001	0.005	0.006
decane	426.171	3.9971	0.0004	0.0005	0.012	water	510.149	57.783	0.001	0.005	0.008
decane	433.470	5.3280	−0.0003	0.0006	0.012	water	518.024	70.102	0.000	0.006	0.007
decane	444.346	7.9913	0.0001	0.0009	0.010	water	525.943	84.504	0.000	0.007	0.009
decane	452.536	10.661	0.001	0.001	0.011	water	533.928	101.300	0.007	0.009	0.015
decane	459.142	13.318	0.000	0.001	0.009	water	541.975	120.76	0.00	0.01	0.026
decane	466.039	16.652	−0.001	0.002	0.008	water	550.075	143.18	−0.01	0.01	0.024
decane	471.764	19.914	−0.001	0.002	0.006	water	558.226	168.90	−0.01	0.01	0.023
decane	479.362	25.034	−0.001	0.002	0.006	water	566.432	198.30	0.00	0.01	0.025
water	486.948	31.164	−0.001	0.003	0.005	water	574.719	231.87	0.01	0.02	0.034
water	494.624	38.553	0.002	0.004	0.006						
Dimethyl Malonate											
decane	351.035	2.0051	0.0000	0.0003	0.053	water	415.739	31.177	0.001	0.003	0.018
decane	364.825	3.9941	0.0001	0.0005	0.025	water	422.084	38.569	0.000	0.004	0.021
decane	371.005	5.3258	−0.0004	0.0007	0.019	water	428.461	47.390	0.002	0.005	0.024
decane	380.198	7.9981	0.0015	0.0009	0.019	water	434.846	57.805	0.004	0.006	0.031
decane	387.080	10.668	0.000	0.001	0.012	water	441.287	70.109	−0.006	0.007	0.042
decane	392.600	13.320	0.000	0.002	0.011	water	447.780[b]	84.497	−0.097	0.008	0.061
decane	398.402	16.680	−0.001	0.002	0.011	water	454.293[b]	101.310	−0.134	0.009	0.080
decane	403.146	19.927	−0.002	0.002	0.010	water	460.824[b]	120.77	−0.17	0.01	0.095
decane	409.421	25.016	0.001	0.002	0.014						

Cyclohexanone Oxime[c]

method	T/K	p/Pa		method	T/K	p/Pa	
IP	330.000	63.741	crystalline[d]	IP	369.999	1179.4	liquid[e]
IP	339.999	144.27	crystalline[d]	IP	375.000	1551.1	liquid[e]
IP	349.999	313.20	crystalline[d]	IP	380.001	2028.2	liquid[e]
IP	360.000	651.31	crystalline[d]	IP	385.001	2620.9	liquid[e]

[a] Inclined piston is (IP). Water (W) or decane (D) refers to which material was used as the standard in the reference ebulliometer. T is the condensation temperature of the sample; the pressure p was calculated from the condensation temperature of the reference substance, and Δp is the difference of the value of pressure, calculated with eq 5 and the parameters listed in Table 10 (p_{Wagner}), from the observed value of pressure ($\Delta p = p - p_{\mathrm{Wagner}}$). σ is the propagated error calculated using $\sigma(p) = (0.001)\{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_x/\mathrm{d}T)^2\}^{1/2}$, where p_{ref} and p_x are the vapor pressures of the reference substance and the compound under study, respectively. ΔT is the difference between the boiling and condensation temperatures ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$) for the sample. [b] Values at this temperature were not included in the fit of the Wagner equation because of sample decomposition that was indicated by the increase in ΔT values. [c] $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}$(cyclohexanone oxime, 345 K) = 76.5 ± 1.0 kJ mol^{-1}. $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(cyclohexanone oxime, 377.5 K) = 63.1 ± 1.0 kJ·mol^{-1}. [d] $\ln(p/1\ \mathrm{Pa}) = 32.0484 - 9205.4/(T/\mathrm{K})$. [e] $\ln(p/1\ \mathrm{Pa}) = 27.5829 - 7588.5/(T/\mathrm{K})$.

The difference between the boiling and condensation temperatures (ΔT) for dimethyl malonate increased significantly above 442 K (see Table 7). Slow decomposition was indicated by the slow increase in ΔT. (See the Discussion for further comments on the stability of dimethyl malonate.)

Inclined-piston vapor-pressure measurements for cyclohexanone oxime are listed in Table 7. For this compound, sample decomposition prevented ebulliometric vapor pressure measurements. Both dicarboxylic acids (glutaric and pimelic) decompose above their respective melting points. As noted in the Introduction, sublimation-pressure measurements using a Knudsen-type effusion apparatus were slated for the research program, but the equipment was not functional in time for completion of the measurements. No ebulliometric or inclined-piston vapor-pressure measurements were attempted on either of those compounds.

Differential Scanning Calorimetry. Table 8 lists equations representing the variation of saturated heat capacity $C_{\mathrm{sat,m}}$ with temperature for the crystalline phase of 1,2,4,5-tetraisopropylbenzene, glutaric and pimelic acids, and cyclohexanone oxime. The derived equations were determined from DSC measurements for various cell fillings. Heat capacities were determined at 20 K intervals with a heating rate of 0.083 K·s^{-1} and a 120 s equilibration period between energy additions (Table 9).

For each of the other compounds, (1,4-diisopropylbenzene, 1,2,4,5-tetraisopropylbenzene (l), and dimethyl malonate), the upper temperature bound of the measurements was set by the critical region. For each of those compounds, an abrupt decrease in the heat capacity associated with the conversion from two phases to one phase was observed. Sample decomposition was greatly reduced by employing a single continuous heat source at a heating rate of 0.333 K·s^{-1}. Temperatures at which conversion to the single phase occurred were measured for several cell fillings. Table 10 reports the density, obtained from the mass of sample and the cell volume,

Table 8. Heat-Capacity Equations and Enthalpies of Fusion Derived from DSC Measurements (R = 8.314 51 J·K^{-1}·mol^{-1})

1,2,4,5-Tetraisopropylbenzene (crystalline)

$C_{\mathrm{sat,m}}/R = 0.1308\ \mathrm{T} + 11.7$ (in temperature range 290 K to 393 K)

$\Delta^{\mathrm{I}}_{\mathrm{cr}}H_{\mathrm{m}}$(1,2,4,5-tetraisopropylbenzene, 393 K) = 19.6 ± 0.5 kJ·mol^{-1}

$\Delta^{\mathrm{I}}_{\mathrm{cr}}H_{\mathrm{m}}$(1,2,4,5-tetraisopropylbenzene, 298.15 K) = 9.2 ± 1.0 kJ·mol^{-1}

Glutaric Acid (cr II)

$C_{\mathrm{sat,m}}/R = 0.077T - 2.33$ (in temperature range 293 K to 338 K)

Glutaric Acid (cr I)

$C_{\mathrm{sat,m}}/R = 0.077T - 2.33$ (in temperature range 338 K to 371 K)

$\Delta^{\mathrm{crI}}_{\mathrm{crII}}H_{\mathrm{m}}$(glutaric acid, 338 K) = 2.4 ± 0.2 kJ·mol^{-1}

$\Delta^{\mathrm{crI}}_{\mathrm{crII}}H_{\mathrm{m}}$(glutaric acid, 298.15 K) = 2.4 ± 0.2 kJ·mol^{-1}

Glutaric Acid (liquid)

$C_{\mathrm{sat,m}}/R = 0.036T + 22.8$ (in temperature range 371 K to 483 K)

$\Delta^{\mathrm{l}}_{\mathrm{crI}}H_{\mathrm{m}}$(glutaric acid, 371 K) = 23.0 ± 0.5 kJ·mol^{-1}

$\Delta^{\mathrm{l}}_{\mathrm{crI}}H_{\mathrm{m}}$(glutaric acid, 298.15 K) = 16.1 ± 1.0 kJ·mol^{-1}

Pimelic Acid (cr II)

$C_{\mathrm{sat,m}}/R = 0.263T - 55.4$ (in temperature range 293 K to 340 K)

Pimelic Acid (cr I)

$C_{\mathrm{sat,m}}/R = 0.263T - 55.4$ (in temperature range 340 K to 377.5 K)

$\Delta^{\mathrm{I}}_{\mathrm{crII}}H_{\mathrm{m}}$(pimelic acid, 340 K) = 1.6 ± 0.2 kJ·mol^{-1}

$\Delta^{\mathrm{I}}_{\mathrm{crII}}H_{\mathrm{m}}$(pimelic acid, 298.15 K) = 1.6 ± 0.2 kJ·mol^{-1}

Pimelic Acid (liquid)

$C_{\mathrm{sat,m}}/R = 0.057\ \mathrm{T} + 23.8$ (in temperature range 377.5 K to 503 K)

$\Delta^{\mathrm{l}}_{\mathrm{crI}}H_{\mathrm{m}}$(pimelic acid, 377.5 K) = 30.3 ± 0.5 kJ·mol^{-1}

$\Delta^{\mathrm{l}}_{\mathrm{crI}}H_{\mathrm{m}}$(pimelic acid, 298.15 K) = 24.0 ± 1.0 kJ·mol^{-1}

Cyclohexanone Oxime (crystalline)

$C_{\mathrm{sat,m}}/R = 0.066T + 2.64$ (in temperature range 290 K to 362.5 K)

Cyclohexanone Oxime (liquid)

$C_{\mathrm{sat,m}}/R = 0.077T + 4.35$ (in temperature range 362.5 K to 460 K)

$\Delta^{\mathrm{l}}_{\mathrm{cr}}H_{\mathrm{m}}$(cyclohexanone oxime, 362.5 K) = 12.7 ± 0.3 kJ·mol^{-1}

$\Delta^{\mathrm{l}}_{\mathrm{cr}}H_{\mathrm{m}}$(cyclohexanone oxime, 298.15 K) = 10.9 ± 1.0 kJ·mol^{-1}

V_x, calculated with eq 4,

$$V_x(T)/V_x(298.15\ \mathrm{K}) = 1 + ay + by^2 \tag{4}$$

where $y = (T - 298.15)$ K, $a = 3.216 \times 10^{-5}$ K^{-1}, and $b = 5.4 \times 10^{-8}$ K^{-2}, and the measured temperatures at which conversion to a single phase was observed.

Critical temperatures and corresponding critical densities were derived graphically for 1,4-diisopropylbenzene, 1,2,4,5-tetraisopropylbenzene, and dimethyl malonate from these results, as seen in Figure 2. The derived values were T_c = (675 ± 1) K with ρ_c = (263 ± 10) kg·m^{-3} for 1,4-diisopropylbenzene, T_c = (703 ± 2) K with ρ_c = (270 ± 30) kg·m^{-3} for 1,2,4,5-tetraisopropylbenzene, and T_c = (647 ± 3) K with ρ_c = (350 ± 15) kg·m^{-3} for dimethyl malonate, respectively. Results of measurements on benzene and toluene performed as "proof-of-concept measurements" for these procedures have been reported.[38] The rapid heating method was used previously for critical temperature and critical density determinations for 2-aminobiphenyl,[39] dibenzothiophene,[40] and carbazole and benzofuran.[41]

Table 9. Two-Phase (Liquid + Vapor) Heat Capacities Derived from DSC Measurements[a] (R = 8.314 51 J·K^{-1}·mol^{-1})

1,4-Diisopropylbenzene

	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$		
T/K	m/g = 0.009 293 $V_c{}^a$ = 0.0528	m/g = 0.013 551 $V_c{}^a$ = 0.0531	m/g = 0.018 366 $V_c{}^a$ = 0.0528
308.15	36.4	36.1	36.1
328.15	38.0	37.6	37.5
348.15	39.4	38.9	39.0
368.15	40.9	40.6	40.6
388.15	42.7	42.1	42.0
408.15	44.0	43.6	43.6
428.15	45.7	45.2	45.1
448.15	47.4	46.7	46.7
468.15	49.4	48.4	48.1
488.15	50.5	50.3	49.7
508.15	52.7	52.1	51.3
528.15	54.7	53.9	52.8
548.15	56.3	55.4	54.4
568.15	58.5	57.2	56.0
588.15	60.8	59.1	57.4
608.15	63.3	61.1	59.2
628.15	66.2	63.3	61.2
648.15	70.8	68.1	63.4
668.15[b]	74.6	74.0	61.2

1,2,4,5-Tetraisopropylbenzene

	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$		
T/K	m/g = 0.009 54 $V_c{}^a$ = 0.0531	m/g = 0.016 24 $V_c{}^a$ = 0.0528	m/g = 0.020 76 $V_c{}^a$ = 0.0528
413.15	69.9	70.3	70.0
433.15	72.0	72.5	72.2
453.15	73.8	74.7	74.4
473.15	76.6	77.1	76.6
493.15	79.6	79.2	78.7
513.15	81.7	81.5	80.8
533.15	84.1	83.7	83.0
553.15	86.9	86.0	84.8
573.15	89.2	88.1	86.5
593.15	91.7	90.4	88.3
613.15	94.5	92.4	91.1
633.15	96.7	94.8	93.0
653.15	96.5	97.0	95.3
673.15	99.9	97.6	99.2
693.15[b]	112.5	107.8	94.3

Dimethyl Malonate

	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$		
T/K	m/g = 0.009 25 $V_c{}^a$ = 0.0528	m/g = 0.013 32 $V_c{}^a$ = 0.0531	m/g = 0.020 98 $V_c{}^a$ = 0.0531
308.15	18.3	17.9	18.1
328.15	18.7	18.2	18.5
348.15	19.1	18.6	18.9
368.15	19.6	19.0	19.2
388.15	20.2	19.5	19.7
408.15	20.8	19.9	20.1
428.15	21.6	20.6	20.7
448.15	22.3	21.5	21.3
468.15	23.0	21.9	21.6
488.15	24.1	22.7	22.2
508.15	25.3	23.6	23.0
528.15	26.9	24.5	23.6
548.15	27.8	25.4	24.5
568.15	29.3	26.6	25.2
588.15	31.2	28.2	26.0
608.15	33.8	30.0	27.2
628.15	33.2	32.2	29.6
648.15[b]	23.3	25.5	25.4

[a] Volume of cell given at 298.15 K. [b] Values not included in fit. Values are listed to show the large drop in heat capacity on passing into the fluid phase.

For 1,2,4,5-tetraisopropylbenzene, glutaric acid, pimelic acid, and cyclohexanone oxime, which were solids at ambient temperature, by judicious choice of starting temperature, the melting endotherm during the DSC enthalpy measurements occurred in the center of a heating cycle. The measured enthalpies during those particular heating cycles contained the enthalpy of fusion plus enthalpies for raising the solid from the initial temperature to the melting point and for raising the liquid from the melting point to the final temperature. The derived enthalpies of fusion for glutaric acid, pimelic acid, and cyclohexanone oxime at their respective melting points and at 298.15 K are reported in Table 8. Polymorphic transitions exist in both dicarboxylic acids. Measurements of the enthalpies were

Table 10. Densities and Temperatures Used To Define the Two-Phase Dome near T_c

ρ/(kg·m^{-3})	T/K	ρ/(kg·m^{-3})	T/K
	1,4-Diisopropylbenzene		
172.5	672.0	286.4	675.0
184.9	672.0	341.0	673.0
250.4	674.7	364.4	672.0
253.1	676.7		
	1,2,4,5-Tetraisopropylbenzene		
170.9	697.7	286.6	703.2
213.5	703.2	330.6	703.2
264.1	703.2	378.4	695.2
	Dimethyl Malonate		
179.0	643.2	417.3	644.7
283.5	648.2	463.7	642.2
327.0	647.7		

made, and corresponding enthalpies of transition are listed in Table 8. Equations, representing the heat capacities for the liquid and solid phases, which were used in the "adjustment" to 298.15 K are also reported in Table 8. (Note: all the heat-capacity equations should only be used to derive values within the temperature ranges specified in Table 8; extrapolation outside the temperature range will produce erroneous values.)

Fitting Procedures. The main goal of the fitting procedures was to derive accurate enthalpies of vaporization for each compound over as wide a temperature range as possible. Although $\Delta_g{}^lH_m$ at 298.15 K is the only value necessary to obtain $\Delta_f H^\circ_m$(g, 298.15 K), the benefit of knowledge of the enthalpy of vaporization over a wide range of temperature was recognized. The exact fitting procedure used for each compound varies depending on the range of measured properties (vapor pressures and heat capacities) available.[41]

For 1,4-diisopropylbenzene, 1,2,4,5-tetraisopropylbenzene, and dimethyl malonate, a simultaneous nonlinear least-squares fit of the vapor pressures listed in Table 7 and the two-phase heat capacities $C^{II}_{X,m}$ given in Table 9 was completed. The fitting procedure has been described in detail,[41] and hence, only a summary of the procedure follows. The fitting parameters were derived by a nonlinear least-squares fit of the vapor pressures listed in Table 7 using the Wagner equation[42] in the formulation given by Ambrose and Walton:[43]

$$\ln(p/p_c) = (1/T_r)[AY + BY^{1.5} + CY^{2.5} + DY^5] \qquad (5)$$

where $T_r = T/T_c$ and $Y = (1 - T_r)$. The vapor-pressure fitting procedure including the minimization equation and the relative weightings is detailed in ref 41. The number of fitting parameters differed depending on whether a critical temperature could be determined experimentally. For each of 1,4-diisopropylbenzene, 1,2,4,5-tetraisopropylbenzene, and dimethyl malonate, a critical temperature was determined from the DSC measurements and, hence, only the critical pressure p_c was included in the variables. For fitting the two-phase heat capacities obtained in a cell of volume V_x, the experimental $C^{II}_{X,m}$ values (Table 2) were converted to $C^{II}_{V,m}$ by means of eq 4 for the cell expansion and the vapor-pressure fit for $(\partial p/\partial T)_{sat}$,

$$C^{II}_{V,m} = C^{II}_{X,m} - T/n\,\{(\partial V_x/\partial T)_x\,(\partial p/\partial T)_{sat}\} \qquad (6)$$

The values of $C^{II}_{V,m}$ were used to derive functions for $(\partial^2 p/\partial T^2)_{sat}$ and $(\partial^2\mu/\cdot T^2)_{sat}$ (see eq 2 of ref 41). The functional form chosen for variation of the second derivative of the chemical potential with temperature was

$$(\partial^2\mu/\partial T^2)_{sat}/(J{\cdot}K^{-2}{\cdot}mol^{-1}) = \sum_{i=0}^{3} b_i(1 - T/T_c)^i \qquad (7)$$

Details of the weighting procedures are given by Steele.[41] Table 11 listed the parameters derived using the procedures outlined above. Details of the fits using the vapor-pressure results are given in Table 7 (column 4 labeled $\Delta p = p - p_{Wagner}$ with p_{Wagner} calculated using the parameters listed in Table 11).

Values of $C^{II}_{V,m}(\rho{=}\rho_{sat})$ were derived for 1,4-diisopropylbenzene, 1,2,4,5-tetraisopropylbenzene, and dimethyl malonate from the parameters listed in Table 11, and corresponding $C_{sat,m}$ values were obtained using eq 6 of ref 41.

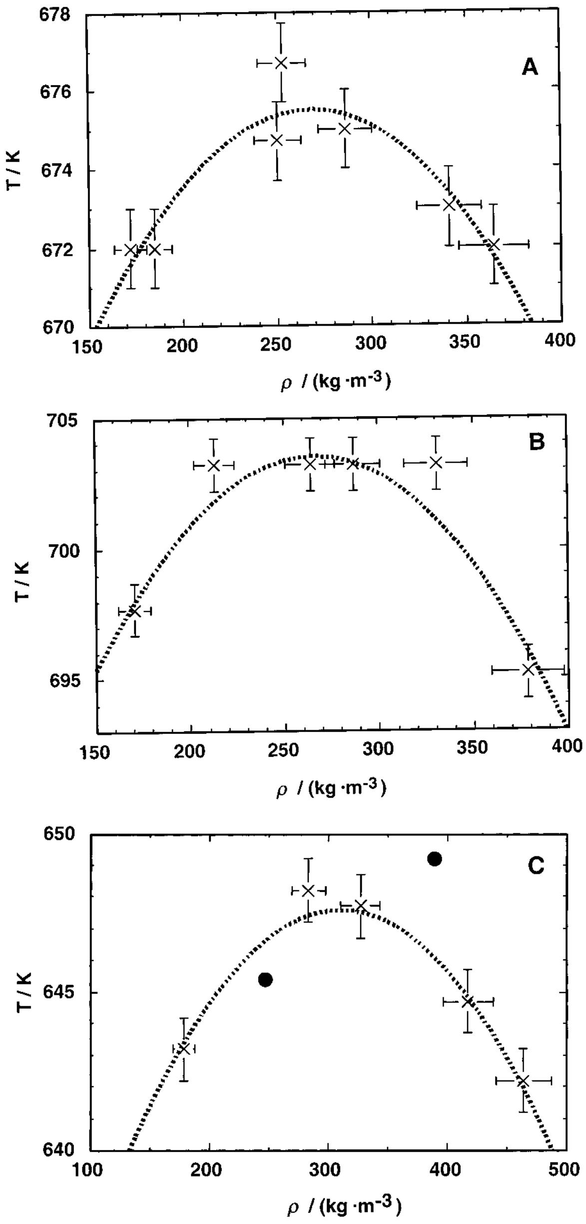


Figure 2. Vapor–liquid coexistence in the region of the critical point. In each part of this figure, the curves are drawn as an aid to the eye and do not represent any theoretically valid equation. The crosses span the range of uncertainty. (A) 1,4-Diisopropylbenzene; (B) 1,2,4,5-tetraisopropylbenzene; (C) dimethyl malonate where ● are results from the measurements of heat capacity, that is, long runs where significant decomposition appeared to occur.

Table 11. Parameters for the Wagner Equation (Eq 5) and for Eq 7, Critical Constants, and Acentric Factors[a]

1,4-Diisopropylbenzene				1,2,4,5-Tetraisopropylbenzene			
A	−8.75355	b_0	−0.66573	A	−9.60536	b_0	−1.01681
B	2.86727	b_1	−0.76565	B	3.45955	b_1	−1.49470
C	−4.37719	b_2	1.04581	C	−6.66997	b_2	2.66241
D	−3.61347	b_3	−1.25241	D	−5.92032	b_3	−3.23915
T_c	675 K	p_c	2330 kPa	T_c	703 K	p_c	1600 kPa
ρ_c	263 kg·m^{-3}	ω	0.4763	ρ_c	270 kg·m^{-3}	ω	0.6480

Dimethyl Malonate			
A	−9.40483	b_0	−0.13369
B	3.40329	b_1	−1.42451
C	−5.10496	b_2	3.09626
D	−4.67592	b_3	−3.19704
T_c	647 K	p_c	3600 kPa
ρ_c	350 kg·m^{-3}	ω	0.5667

[a] The parameters listed in this table are those derived using the procedures detailed in the text.

Table 12. Values of $C_{sat,m}/R$ (R = 8.314 51 J·K^{-1}·mol^{-1})

T/K	$C_{sat,m}/R$	T/K	$C_{sat,m}/R$
1,4-Diisopropylbenzene			
300.0	35.5	480.0	48.5
320.0	37.0	500.0	49.9
340.0	38.5	520.0	51.3
360.0	40.0	540.0	52.7
380.0	41.4	560.0	54.0
400.0	42.9	580.0	55.5
420.0	44.3	600.0	57.1
440.0	45.7	620.0	59.0
460.0	47.1	640.0	62.0
1,2,4,5-Tetraisopropylbenzene			
410.0	69.7	570.0	85.7
430.0	71.7	590.0	87.5
450.0	73.8	610.0	89.2
470.0	75.9	630.0	91.0
490.0	77.9	650.0	93.1
510.0	80.0	670.0	96.3
530.0	81.9	690.0	105.7
550.0	83.9		
Dimethyl Malonate			
300.0	18.1	480.0	21.1
320.0	18.3	500.0	21.5
340.0	18.6	520.0	21.7
360.0	18.9	540.0	21.9
380.0	19.2	560.0	22.1
400.0	19.6	580.0	22.4
420.0	20.0	600.0	23.1
440.0	20.4	620.0	25.8
460.0	20.8		

Table 13. Enthalpies of Vaporization Obtained from the Wagner and Clapeyron Equations[a]

T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}
1,4-Diisopropylbenzene			
298.15[b]	56.93 ± 0.23	440.0	46.25 ± 0.28
300.0[b]	56.78 ± 0.23	460.0	44.68 ± 0.37
320.0[b]	55.18 ± 0.22	480.0	43.02 ± 0.50
340.0[b]	53.65 ± 0.20	500.0	41.24 ± 0.65
360.0[b]	52.16 ± 0.18	520.0	39.34 ± 0.85
380.0	50.69 ± 0.18	540.0[b]	37.3 ± 1.1
400.0	49.24 ± 0.18	560.0[b]	35.0 ± 1.3
420.0	47.77 ± 0.22	580.0[b]	32.6 ± 1.6
1,2,4,5-Tetraisopropylbenzene			
298.15[b,c]	75.69 ± 0.45	500.0	52.30 ± 0.48
360.0	67.84 ± 0.32	520.0	49.95 ± 0.65
380.0[b,c]	65.50 ± 0.28	540.0	47.48 ± 0.85
400.0[b]	63.26 ± 0.27	560.0	44.9 ± 1.1
420.0	61.06 ± 0.25	580.0[b]	42.1 ± 1.4
440.0	58.91 ± 0.25	600.0[b]	39.1 ± 1.7
460.0	56.75 ± 0.28	620.0[b]	35.8 ± 2.0
480.0	54.56 ± 0.37		
Dimethyl Malonate			
298.15[b]	58.48 ± 0.27	420.0	47.78 ± 0.25
300.0[b]	58.29 ± 0.27	440.0	46.05 ± 0.33
320.0[b]	56.40 ± 0.23	460.0	44.25 ± 0.45
340.0[b]	54.58 ± 0.22	480.0[b]	42.33 ± 0.62
360.0	52.85 ± 0.20	500.0[b]	40.28 ± 0.80
380.0	51.15 ± 0.20	520.0[b]	38.1 ± 1.0
400.0	49.47 ± 0.20		

Cyclohexanone Oxime[d]

$\Delta_{cr}^{g}H_m$(cyclohexanone oxime, 345 K) = 76.5 ± 1.0 kJ·mol^{-1}

$\Delta_{l}^{g}H_m$(cyclohexanone oxime, 377.5 K) = 63.1 ± 1.0 kJ·mol^{-1}

$\Delta_{cr}^{l}H_m$(cyclohexanone oxime, 362.5 K) = 12.7 ± 0.3 kJ·mol^{-1}

$\Delta_{cr}^{l}H_m$(cyclohexanone oxime, 298.15 K) = 10.9 ± 1.0 kJ·mol^{-1}

$\Delta_{cr}^{g}H_m$(cyclohexanone oxime, 298.15 K) = 79.0 ± 2.0 kJ·mol^{-1} [d,f]

$\Delta_{cr}^{g}H_m$(cyclohexanone oxime, 298.15 K) = 80.2 ± 2.0 kJ·mol^{-1} [e,f]

[a] Uncertainty intervals are twice the standard deviation of the mean. [b] The value at this temperature was calculated with extrapolated vapor pressures derived from the fitted Wagner equation. [c] The value at this temperature represents the metastable (supercooled) liquid. [d] Derived from the vaporization + fusion path. [e] Derived from the sublimation path. [f] Average of *d* and *e* used in Table 14 to avoid confusion in this table of two different values for the same property.

The results for $C_{sat,m}/R$ are reported in Table 12. The estimated uncertainty in these values is 1%.

Enthalpies of vaporization $\Delta_l^g H_m$ (Table 13) were derived from the Wagner-equation fits using the Clapeyron equation:

$$\mathrm{d}p/\mathrm{d}T = \Delta_l^g H_m/(T\Delta_l^g V_m) \qquad (8)$$

where $\Delta_l^g V_m$ is the increase in molar volume from the liquid to the real vapor. Estimates of the liquid-phase molar volumes, V_m(l), were made with the extended corresponding-states equation of Riedel,[44] as formulated by Hales and Townsend:[45]

$$(\rho/\rho_c) = 1.0 + 0.85Y + (1.6916 + 0.9846\omega)Y^{1/3} \qquad (9)$$

with $Y = (1 - T/T_c)$, ρ_c = critical density, and ω = acentric factor. The acentric factor, ω, is defined as $[-\log(p/p_c) - 1]$, where p is the vapor pressure at $T/T_c = 0.7$ and p_c is the critical pressure. A value for ω was obtained from the vapor-pressure fitting parameters and a corresponding value of ρ_c derived from the liquid-phase density measurement. Vapor-phase volumes were calculated with the virial equation of state truncated at the third virial coefficient. Second virial coefficients were estimated with the corresponding-states equation of Pitzer and Curl,[46] and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera.[47] This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene and toluene.[38] Third virial coefficients are required for accurate calculation of the gas volume for pressures greater than 1 bar. Uncertainties in the virial coefficients are assumed to be 10% of the respective numerical values. Derived enthalpies of vaporization are reported in Table 13. For $p > 1$ bar, the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived enthalpies of vaporization.

For cyclohexanone oxime, which decomposed well below the critical region and for which the measured vapor pressures covered a relatively narrow range of temperature (Table 7), all estimating procedures (see, e.g., ref 9) gave

Table 14. Thermochemical Properties at 298.15 K (R = 8.314 51 J·K^{-1}·mol^{-1} and p° = 101.325 kPa)

compd	$\Delta_f H^\circ_m$(c)/kJ·mol^{-1}	$\Delta_c^l H^\circ_m$/kJ·mol^{-1}	$\Delta_f H^\circ_m$(l)/kJ·mol^{-1}	$\Delta_l^g H^\circ_m$/kJ·mol^{-1}	$\Delta_f H^\circ_m$(g)/kJ·mol^{-1}
1,4-diisopropylbenzene			−130.07 ± 1.22	56.93 ± 0.23	−73.1 ± 1.2
1,2,4,5-tetraisopropylbenzene	−297.4 ± 2.0	9.2 ± 1.0	−288.2 ± 2.2	75.69 ± 0.45	−212.5 ± 2.2
dimethyl malonate			−797.50 ± 0.44	58.48 ± 0.27	−739.0 ± 0.5
glutaric acid	−958.84 ± 0.54	18.5 ± 1.1	−940.3 ± 1.2	103 ± 8[a,b]	−837 ± 8
pimelic acid	−1017.1 ± 0.8	25.6 ± 1.0	−991.5 ± 1.3		
cyclohexanone oxime	−152.41 ± 0.76	10.9 ± 1.0	−141.5 ± 1.3	68.7 ± 1.5	−72.8 ± 2.0

[a] The value at this temperature represents the metastable (supercooled) liquid. [b] See text for details of determination of the value.

unrealistic values for the critical pressure. Simplified forms of the vapor pressure equation

$$\ln(p(\mathrm{cr})/1\ \mathrm{Pa}) = 32.048 - 9205.4/(T/\mathrm{K}) \tag{10}$$

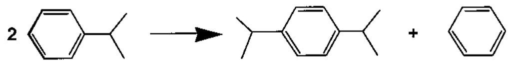
$$\ln(p(\mathrm{l})/1\ \mathrm{Pa}) = 27.583 - 7588.5/(T/\mathrm{K}) \tag{10A}$$

with p_{ref} = 1 Pa were derived for the crystalline and liquid phases, respectively. Corresponding enthalpies of sublimation, $\Delta_{cr}^{g}H_m$, and vaporization, $\Delta_{l}^{g}H_m$, at the respective mean temperatures were derived and are listed in Table 7. Enthalpies of sublimation and vaporization at 298.15 K were derived by combining those results with the heat-capacity measurements in Table 8. Values are listed in Table 13.

Ideal-Gas Enthalpies of Formation. Table 14 summarizes the thermochemical property measurements and derived ideal-gas standard enthalpies of formation for all the compounds of this study. The enthalpies of vaporization, $\Delta_{l}^{g}H_m$, at 298.15 K reported in Table 13 were converted to the corresponding values for the ideal gas, $\Delta_{l}^{g}H^\circ_m$, using estimated ($H^\circ - H$) values for the real gas at its saturation vapor pressure at 298.15 K. The estimates were calculated using eq 20 of ref 48 and the virial coefficients derived as described above. For all the compounds of this study, the corrections were calculated to be negligibly small.

Discussion

1,4-Diisopropylbenzene. No previous studies on the energy of combustion of 1,4-diisopropylbenzene were found in a search of the literature via Chemical Abstracts through June 1997. Popov et al.[49] studied the disproportionation equilibrium of isopropylbenzene and list $\Delta_r H^\circ_m$ = (1.5 ± 0.63) kJ·mol^{-1} for the reaction



in the temperature range 313 K to 373 K. Neglecting any enthalpy correction from the mean temperature 343 K to 298.15 K and combining the listed enthalpy of reaction with the standard enthalpies of formation of isopropylbenzene (l) and benzene (l) recommended by Pedley,[14] −(41.1 ± 1.0) kJ·mol^{-1} and (49.0 ± 0.6) kJ·mol^{-1}, respectively, give $\Delta_f H^\circ_m(\mathrm{C_{12}H_{18}}$, l) = −(129.5 ± 1.7) kJ·mol^{-1} for 1,4-diisopropylbenzene, in excellent agreement with the value $\Delta_f H^\circ_m(\mathrm{C_{12}H_{18}}$, l) = −(130.07 ± 1.22) kJ·mol^{-1} determined in this research (Table 14).

As detailed above in the text and in Table 11, values for the critical properties T_c = (675 ± 1) K with ρ_c = (263 ± 10) kg·m^{-3} and p_c = (2330 ± 100) kPa were derived for 1,4-diisopropylbenzene. Dreisbach[79] lists T_c = 675 K with ρ_c = 278 kg·m^{-3} and p_c = 2360 kPa. Using the estimation scheme due to Joback,[50] the corresponding estimated values are T_c = 683 K with ρ_c = 276 kg·m^{-3} and p_c = 2410 kPa.

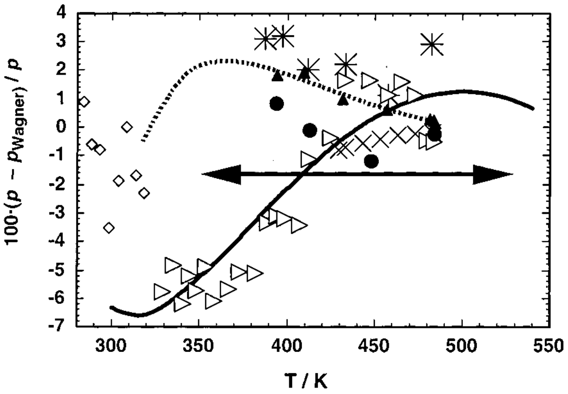


Figure 3. Comparison of literature vapor pressures for 1,4-diisopropylbenzene with values obtained using the Wagner equation (eq 5) and the parameters listed in Table 10. The double-headed arrow represents the temperature span of the vapor pressure measurements obtained in this research (Table 7). The solid line represents the DIPPR Project 801 correlation equation.[56] The dashed line represents the calculated vapor pressures given in Table 3 of McDonald et al.[55] Key: ▲, actual experimental vapor pressure measurements of McDonald et al.;[55] ×, Newton;[51] ∗, Stull;[52] ●, Melpolder et al.;[53] triangle pointing right, Myers and Fenske;[54] ◇, Verevkin.[59]

Vapor-pressure measurements in the temperature range 408 K to 485 K on 1,4-diisopropylbenzene were reported by Newton,[51] Stull[52] (in Table 1 of ref 52, the compound is referred to as 1,2-diisopropylbenzene, but that is corrected to 1,4-diisopropylbenzene in the subsequent errata), Melpolder et al.,[53] Myers and Fenske,[54] and McDonald et al.[55] In addition to the actual measured values, the Dow group[55] published values at set pressures in the range 1 to 760 mmHg (their Table 3). Both the “raw data” and the interpolated values are compared in Figure 3 with values obtained using the Wagner equation, eq 5, and the parameters listed in Table 11. McDonald et al. state in their Table 1 “The data above 300 mmHg are more reliable than those below”. Results shown in Figure 3 are in accord with this statement. Also given in Figure 3 is a solid line representing the DIPPR Project 801 Database correlation equation.[56] The correlation equation was probably derived giving great weight to the values of Myers and Fenske.[54] (Daubert et al.[56] missed abstracting from the literature the results of the study by Newton[51] and the Dow vapor pressure data of McDonald et al.[55])

An equation representing the saturation liquid-phase density of 1,4-diisopropylbenzene in the temperature range 292.8 K to 344 K was derived by Newton.[51] Density values calculated using the extended corresponding states equation (eq 7) and the parameters listed in Table 11 are within 0.1% of those obtained using Newton’s equation.

Estimation of the ideal-gas enthalpy of formation of 1,4-diisopropylbenzene follows. Using the group parameters given in refs 8 and 9,

4	$C_b-(C_b)_2(H)$	$13.82 \times 4 = 55.28$
2	$C_b-(C_b)_2(C)$	$23.07 \times 2 = 46.14$
2	$C-(C_b)(C)_2(H)$	$-4.10 \times 2 = -8.20$
4	$C-(C)(H)_3$	$-42.25 \times 4 = -169.0$

hence

$$\Delta_f H^\circ_m(C_{12}H_{18}, \text{g}, 298.15\ \text{K}) = -75.8\ \text{kJ·mol}^{-1}$$

This is in reasonably good agreement with the value $\Delta_f H^\circ_m(C_{12}H_{18}$, g, 298.15 K) = −(73.1 ± 1.2) kJ·mol^{-1} obtained in this research (Table 14). It is probable that the $C-(C_b)(C)_2(H)$ group value was derived from just the one enthalpy of formation, namely that of isopropylbenzene, −(41.1 ± 1.0) kJ·mol^{-1} (see ref 14). Combining both isopropylbenzene and 1,4-diisopropylbenzene results gives a new value of −3.2 kJ·mol^{-1} for the ideal-gas enthalpy of formation of the $C-(C_b)(C)_2(H)$ group. Recalculation of the above using the revised group value gives $\Delta_f H^\circ_m(C_{12}H_{18}$, g, 298.15 K) = −74.0 kJ·mol^{-1}, which is in better agreement with the experimentally derived value.

1,2,4,5-Tetraisopropylbenzene. Other than a couple of single-temperature density measurements, approximately 50 melting point determinations, and approximately the same number of single-point boiling point determinations found in a Beilstein and Chemical Abstracts search through June 1997, no thermochemical or thermophysical property measurements were found for 1,2,4,5-tetraisopropylbenzene.

As outlined above, values for the critical properties T_c = (703 ± 2) K with ρ_c = (270 ± 30) kg·m^{-3} and p_c = (1600 ± 300) kPa were derived for 1,2,4,5-tetraisopropylbenzene. Using the estimation scheme due to Joback,[50] the corresponding estimated values are T_c = 699 K with ρ_c = 270 kg·m^{-3} and p_c = 1450 kPa. In a search of the literature, no experimentally determined critical point values were obtained for comparison.

Estimation of the ideal-gas enthalpy of formation of 1,2,4,5-tetraisopropylbenzene follows. Using the group parameters given in refs 8 and 9 and the $C-(C_b)(C)_2(H)$ group value from above,

2	$C_b-(C_b)_2(H)$	$13.82 \times 2 = 27.64$
4	$C_b-(C_b)_2(C)$	$23.07 \times 4 = 92.28$
4	$C-(C_b)(C)_2(H)$	$-3.20 \times 4 = -12.8$
8	$C-(C)(H)_3$	$-42.25 \times 8 = -338.0$

hence

$$\Delta_f H^\circ_m(C_{18}H_{30}, \text{g}, 298.15\ \text{K}) = -230.9\ \text{kJ·mol}^{-1}$$

neglecting the two ortho interaction terms.

The derived ideal-gas enthalpy of formation (Table 14) is $\Delta_f H^\circ_m(C_{18}H_{30}$, g, 298.15 K) = −(212.5 ± 2.2) kJ·mol^{-1}. The ortho interaction term, 9.2 kJ·mol^{-1}, is considerably higher than that given in either ref 8 or 9, 2.4 kJ·mol^{-1}. It should be remembered that the ortho group correction listed in the tables of group additivity values was probably derived from a small database that contained benzenes with substituents no larger than methyl or ethyl. A quick cursory Chemical Abstracts search found ideal-gas enthalpies of formation for only 1,2-dimethylbenzene, 1-ethyl-2-methylbenzene, 1,2,3-trimethylbenzene, and 1,2,4-trimethylbenzene as compounds from which to derive the ortho group correction. These data sets could be expanded to include several more compounds, all with the formula $C_{10}H_{14}$, on which careful combustion calorimetric studies were performed by Bill Good of the Bartlesville laboratory and reported in refs 57 and 58, if values for the respective enthalpies of vaporization at 298.15 K became available.

Note in Proof. Prior to submission of this paper to JCED, a search of the literature through January 2001 produced a paper on the thermochemical properties of isopropylbenzenes (1,3-di-, 1,4-di-, and 1,3,5-tri-) by Verevkin.[59] The value for the enthalpy of combustion of 1,4-diisopropylbenzene obtained by Verevkin $\Delta_c H^\circ_m(C_{12}H_{18}$, l, 298.15 K) = −(7162.74 ± 0.98) kJ·mol^{-1} is in good agreement with that obtained here, $\Delta_c H^\circ_m(C_{12}H_{18}$, l, 298.15 K) = −(7164.52 ± 1.04) kJ·mol^{-1} (see Table 6). Verevkin[59] measured vapor pressures in the temperature region 283.7 K to 318.3 K using the transpiration method and derived enthalpies of vaporization for the midtemperature point (301 K) and for 298.15 K. The measured vapor pressures are compared in Figure 3 with values obtained using the Wagner equation, eq 5, and the parameters listed in Table 11. Agreement is scattered. However, Verevkin[59] derived a value for the enthalpy of vaporization of 1,4-diisopropylbenzene, $\Delta_l^g H_m(C_{12}H_{18}$, 298.15 K) = (56.49 ± 0.27) kJ·mol^{-1}, which is in *good* agreement with that derived from the Wagner-equation fit using the Clapeyron equation (eq 6 above), $\Delta_l^g H_m(C_{12}H_{18}$, 298.15 K) = (56.93 ± 0.23) kJ·mol^{-1} (Table 13).

Comparison of the ideal-gas enthalpies of formation for both 1,3-diisopropylbenzene and 1,3,5-triisopropylbenzene as determined by Verevkin with the corresponding group-additivity estimates follows. Using the group parameters given in refs 8 and 9 and the $C-(C_b)(C)_2(H)$ group value from above, for 1,3-diisopropylbenzene

4	$C_b-(C_b)_2(H)$	$13.82 \times 4 = 55.28$
2	$C_b-(C_b)_2(C)$	$23.07 \times 2 = 46.14$
2	$C-(C_b)(C)_2(H)$	$-3.20 \times 2 = -6.40$
4	$C-(C)(H)_3$	$-42.25 \times 4 = -169.0$

hence

$$(\Delta_f H^\circ_m(C_{12}H_{18}, \text{g}, 298.15\ \text{K}) = -74.0\ \text{kJ·mol}^{-1}$$

The derived ideal-gas enthalpy of formation (Table 5 of ref 59) is $\Delta_f H^\circ_m(C_{12}H_{18}$, g, 298.15 K) = −(75.4± 1.3) kJ·mol^{-1}. The agreement is excellent.

For 1,3,5-triisopropylbenzene

3	$C_b-(C_b)_2(H)$	$13.82 \times 3 = 41.46$
3	$C_b-(C_b)_2(C)$	$23.07 \times 3 = 69.21$
3	$C-(C_b)(C)_2(H)$	$-3.20 \times 3 = -9.60$
6	$C-(C)(H)_3$	$-42.25 \times 6 = -253.5$

hence

$$\Delta_f H^\circ_m(C_{12}H_{18}, \text{g}, 298.15\ \text{K}) = -152.4\ \text{kJ·mol}^{-1}$$

The derived ideal-gas enthalpy of formation (Table 5 of ref 59) is $\Delta_f H^\circ_m(C_{15}H_{24}$, g, 298.15 K) = −(154.6± 1.5) kJ·mol^{-1}. The agreement is again excellent.

Dimethyl Malonate. Two previous determinations of the enthalpy of combustion of dimethyl malonate[60−62] were found in a search of the literature through June 1997. The values for the enthalpy of combustion obtained by Verkade et al., $\Delta_c H^\circ_m(C_5H_8O_4$, l, 298.15 K) = −(2318.9 ± 1.5) kJ·mol^{-1}, and by Verevkin et al. $\Delta_c H^\circ_m(C_5H_8O_4$, l, 298.15 K) = −(2311.2 ± 0.6) kJ·mol^{-1}, span that obtained here, $\Delta_c H^\circ_m(C_5H_8O_4$, l, 298.15 K) = −(2313.37 ± 0.32) kJ·mol^{-1} (see Tables 5 and 6). Because of a misinterpretation, the NIST Webbook[63] states that the energy of combustion measured by Verkade et al.[60] is for the solid at 15 °C. In

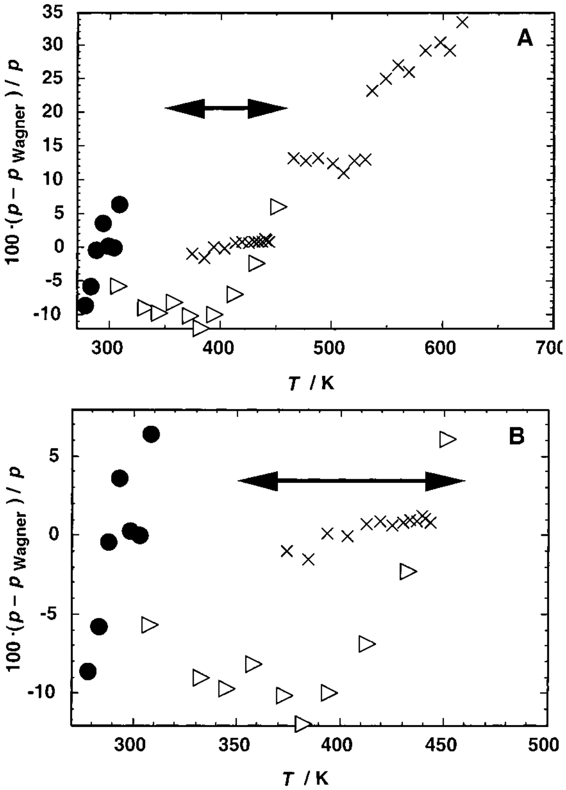


Figure 4. Comparison of literature vapor pressures for dimethyl malonate with values obtained using the Wagner equation (eq 5) and the parameters listed in Table 11. Part B is an expansion of a section of part A to clarify the comparisons. The double-headed arrow represents the temperature span of the vapor-pressure measurements obtained in this research (Table 7). Key: triangle pointing right, Stull;[52] ×, Askonas and Daubert;[64] ●, Verevkin et al.[62]

reality the measurements were made in terms of the 15 °C calorie for the liquid phase at 20 °C.

As outlined above, values for the critical properties $T_c = (647 \pm 3)$ K with $\rho_c = (350 \pm 15)$ kg·m^{-3} and $p_c = (3600 \pm 300)$ kPa were derived for dimethyl malonate. Using the estimate scheme due to Joback,[50] the corresponding estimated values are $T_c = 647$ K with $\rho_c = 359$ kg·m^{-3} and $p_c = 3510$ kPa. In a search of the literature, no experimentally determined critical point values were obtained for comparison.

Stull,[52] Askonas and Daubert,[64] and Verevkin et al.[62] reported vapor-pressure measurements on dimethyl malonate. Parts A and B of Figure 4 compare the measurements found in the literature search with values obtained using the Wagner equation, eq 5, and the parameters listed in Table 11. Stull[52] lists values for the vapor pressure of dimethyl malonate which are probably only of historic interest obtained by Anschûtz and Reitter in the mid 1890s. Askonas and Daubert[64] made measurements over a wide temperature/pressure range, noting that the low- and high-pressure data agreed very well and the best fit was to a ln(p) versus (1/T) vapor pressure equation omitting just the highest temperature/pressure point from the regression. Within the temperature range 374 K to 443 K (6 kPa to 74.75 kPa), agreement between the Askonas and Daubert values and those obtained using the Wagner equation, eq 5, and the parameters listed in Table 11 is excellent. At higher temperature, the agreement is not good and appears to show decomposition of the sample (see Figure 4A). Agreement between the measurements of Verevkin et al.[62] and values extrapolated using the Wagner equation, eq 5, and the parameters listed in Table 11 is also excellent. The scatter, see Figure 4B, is probably a measure of the precision of the evaporation flow (transpiration) method used in the Verevkin et al. determinations.

Verevkin et al.[62] derived a value for the enthalpy of vaporization of dimethyl malonate. The value $\Delta_l^g H_m$($C_5H_8O_4$, 298.15 K) = (61.84 ± 0.79) kJ·mol^{-1} is in poor agreement with that derived from the Wagner-equation fit using the Clapeyron equation (eq 6 above): $\Delta_l^g H_m$($C_5H_8O_4$, 298.15 K) = (58.48 ± 0.27) kJ·mol^{-1} (Table 13). Although the absolute vapor-pressure values are in good agreement, the temperature dependences of the respective data sets are clearly discordant, which is reflected in the poor agreement between the enthalpy-of-vaporization values.

Estimation of the ideal-gas enthalpy of formation of dimethyl malonate follows. Using the group parameters derived within this project,

2	C−(O)(H)$_3$	−42.25 × 2 = −84.50
2	O−(CO)(C)	−179.70 × 2 = −359.40
2	CO−(O)(C)	−146.96 × 2 = −293.92
	C−(CO)$_2$(H)$_2$	???

$$\Delta_f H_m^\circ(C_5H_8O_4, \text{g}, 298.15\ \text{K}) = -739.0\ \text{kJ·mol}^{-1}$$

Hence the C−(CO)$_2$(H)$_2$ group-additivity parameter equals −1.2 kJ·mol^{-1}.

In their paper, Verevkin et al.[62] detail the use a semimicrobomb calorimeter to measure the energy of combustion of diethyl malonate and, hence, the enthalpies of formation for both the liquid and ideal-gas phases. However, in a personal communication between Sergey Verevkin and an author (R.D.C.), it was established that the compound studied was *not* diethyl malonate. Therefore, the results listed in ref 62 could not be used to confirm the new group parameter.

Glutaric Acid. Glutaric acid became a compound under study in this project mainly to determine the ideal-gas-phase enthalpy of formation and derive group-additivity functions applicable to dicarboxylic acids. Three previous determinations of the enthalpy of combustion of glutaric acid[65−67] were found in a search of the literature through June 1997. All three are in good agreement with each other [$\Delta_c H_m^\circ$($C_5H_8O_4$, cr, 298.15 K) = −(2151.6 ± 5.0) kJ·mol^{-1}, $\Delta_c H_m^\circ$($C_5H_8O_4$, cr, 298.15 K) = −(2150.9 ± 1.2) kJ·mol^{-1}, $\Delta_c H_m^\circ$($C_5H_8O_4$, cr, 298.15 K) = −(2150.4 ± 0.8) kJ·mol^{-1}, respectively] and also with the value $\Delta_c H_m^\circ$($C_5H_8O_4$, cr, 298.15 K) = −(2152.03 ± 0.46) kJ·mol^{-1}, obtained here (see Tables 5 and 6).

A crystalline phase transition at 338 K prior to melting at 371 K was found during the DSC heat-capacity measurements on glutaric acid. Jagannathan and Rao[68] showed clear evidence of structural changes accompanying the transition. However, the heat-capacity values obtained in this research on either side of the transition correlated with the same equation $C_{sat,m}/R = 0.077T - 2.33$ (see Table 8). A value for the enthalpy of the transition of $\Delta_{crII}^{crI} H_m$(glutaric acid, 338 K) = 2.4 ± 0.2 kJ mol^{-1} was obtained (see Table 8). Measurements gave a value for the enthalpy of fusion of $\Delta_{crI}^{l} H_m$(glutaric acid, 371 K) = 23.0 ± 0.5 kJ mol^{-1} (Table 8). Petropavlov et al.[69] determined a transition for glutaric acid at 338 K with the enthalpy of transition 2.4 kJ mol^{-1}. In a DSC study of phase transitions in aliphatic dicarboxylic acids, Cingolani and Berchiesi[70] measured an enthalpy of transition of 2.464 kJ mol^{-1} at 348.5 K and an enthalpy of fusion of 20.9 kJ mol^{-1} for a fusion temperature of 371.0 K.

Table 15. Enthalpies of Vaporization for Glutaric Acid Derived Using Literature Vapor Pressures[a]

T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}
298.15	103 ± 8	500.0	92 ± 8
400.0	96 ± 8	520.0	91 ± 8
420.0	95 ± 8	540.0	90 ± 8
440.0	94 ± 8	560.0	89 ± 8
460.0	93 ± 8	580.0	87 ± 8
480.0	93 ± 8	600.0	85 ± 8

[a] See text.

As noted in the Introduction, an effusion apparatus was never completely functional in time for completion of measurements on the dicarboxylic acids within this project. The following section describes the use of literature values in the derivation of enthalpies of vaporization for glutaric acid.

A search of the literature revealed a set of vapor-pressure measurements (temperatures at set pressures) listed by Stull[52] which he obtained using his correlation method from data attributed to 1889 measurements by Krafft and Noerdlinger.[71] An Antoine equation of the form

$$\lg(p/p_{\mathrm{ref}}) = 9.6846 - 4144.87/[(T/\mathrm{K}) - 36.21] \quad (11)$$

with $p_{\mathrm{ref}} = 1$ kPa was derived using the Stull vapor pressures and enthalpies of vaporization determined as follows. Second virial coefficients were estimated with the correlation of Scott et al.[72] Since enthalpies of vaporization were not derived for pressures greater than 1 bar, third virials were neglected. Liquid-phase volumes were derived using the densities determined at 5 K intervals in the temperature range 373 K to 423 K by Khetarpal et al.[73] The derived enthalpies of vaporization are reported in Table 15. Uncertainties in the virial coefficients were assumed to be 20%. The extrapolation to give the listed enthalpy of vaporization at 298.15 K for the supercooled liquid is long and, in addition, no allowance has been made for the possibility of association at the lower temperatures, so the value is probably a lower limit. However, in the absence of actual vapor-pressure measurements in the region of 298.15 K, the value is used in Table 14 to derive an ideal-gas standard enthalpy of formation for glutaric acid.

Estimation of the ideal-gas enthalpy of formation of glutaric acid follows. Using the group parameters,

2	$O-(CO)(H)$	$-243.25 \times 2 = -486.50$
2	$CO-(O)(C)$	$-146.96 \times 2 = -293.92$
1	$C-(C)_2(H)_2$	$-20.21 \times 1 = -20.21$
2	$C-(CO)(C)(H)_2$	$-21.80 \times 2 = -43.60$

$$\Delta_f H_m^\circ(C_5H_8O_4, \mathrm{g}, 298.15\ \mathrm{K}) = -844.2\ \mathrm{kJ \cdot mol^{-1}}$$

This is in good agreement with the value $\Delta_f H_m^\circ(C_5H_8O_4$, g, 298.15 K$) = -(837 \pm 8)$ kJ·mol^{-1} obtained in this research (Table 14).

Pimelic Acid. Like its homologue glutaric acid, pimelic acid became a compound under study in this project mainly to determine the ideal-gas-phase enthalpy of formation and derive group-additivity functions applicable to dicarboxylic acids. A previous determination of the enthalpy of combustion of pimelic acid[65] was found in a search of the literature through June 1997. The value, corrected to modern units from the 15° calorie upon which it was based, $\Delta_c H_m^\circ(C_7H_{12}O_4$, cr, 298.15 K$) = -(3460 \pm 5)$ kJ·mol^{-1}, is in reasonably good agreement with the value $\Delta_c H_m^\circ(C_7H_{12}O_4$, cr, 298.15 K$) = -(3452.45 \pm 0.68)$ kJ·mol^{-1} obtained here (see Tables 5 and 6).

Two crystalline phase transitions, at 340 K and approximately 373 K, prior to melting at 377 K were found during the DSC heat-capacity measurements on pimelic acid. Jagannathan and Rao[68] showed clear evidence of structural changes accompanying the lower transition that they assigned to 348 K. However, as was the case of glutaric acid, the heat-capacity values obtained in this research on either side of the lower transition correlated with the same equation $C_{\mathrm{sat,m}}/R = 0.263T - 55.4$ (see Table 8). A value for the enthalpy of the transition of $\Delta_{\mathrm{crII}}^{\mathrm{crI}} H_m$(pimelic acid, 340 K) = (1.6 ± 0.2) kJ mol^{-1} was obtained (see Table 8). The DSC measurements were made in a manner that did not facilitate the separation of an enthalpy for the transition at approximately 373 K from that of the fusion. Therefore, the value for that enthalpy was included in that obtained for the melting, giving an overall "enthalpy of fusion" of $\Delta_{\mathrm{crI}}^{\mathrm{l}} H_m$(pimelic acid, 377.5 K) = (30.3 ± 0.5) kJ mol^{-1} (Table 8). Petropavlov et al.[69] determined a transition for pimelic acid at 369.7 K with an enthalpy of transition 1.0 kJ mol^{-1}. In a DSC study of phase transitions in aliphatic dicarboxylic acids, Cingolani and Berchiesi[70] measured an enthalpy for the upper transition of 1.322 kJ mol^{-1} at 369.0 K and an enthalpy of fusion of 27.6 kJ mol^{-1} for a fusion temperature of 377.5 K, in reasonable agreement with the sum of 30.3 kJ mol^{-1} obtained here.

As per glutaric acid, a search of the literature revealed a set of vapor-pressure measurements (temperatures at set pressures) listed by Stull[52] for pimelic acid that he obtained using his correlation method from data attributed to Krafft and Noerdlinger.[71] An Antoine equation of the form

$$\lg(p/p_{\mathrm{ref}}) = 8.600 - 3867.00/[(T/\mathrm{K}) - 28.78] \quad (12)$$

with $p_{\mathrm{ref}} = 1$ kPa was derived using the Stull vapor pressures. Using the same method as that outlined above for glutaric acid, enthalpies of vaporization were derived. The enthalpies of vaporization were abnormally low in comparison to those obtained above for glutaric acid, preventing any assignment of values for this compound.

Estimation of the ideal-gas enthalpy of formation of pimelic acid follows. Using the group parameters

2	$O-(CO)(H)$	$-243.25 \times 2 = -486.50$
2	$CO-(O)(C)$	$-146.96 \times 2 = -293.92$
3	$C-(C)_2(H)_2$	$-20.21 \times 3 = -60.63$
2	$C-(CO)(C)(H)_2$	$-21.80 \times 2 = -43.60$

$$\Delta_f H_m^\circ(C_7H_{12}O_4, \mathrm{g}, 298.15\ \mathrm{K}) = -884.7\ \mathrm{kJ \cdot mol^{-1}}$$

For exact agreement between the group-additivity calculation of the ideal-gas enthalpy of formation and that derived using the results of this research, an enthalpy of sublimation, $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m(C_7H_{12}O_4$, 298.15 K$) = 132.5$ kJ mol^{-1}, would be required.

Note in Proof. Prior to submission of this paper to JCED, a search of the literature through January 2001 produced a paper on the vapor pressures and enthalpies of sublimation of five dicarboxylic acids by Ribeiro da Silva et al.[80] Both glutaric and pimelic acids were included in the study. The enthalpy of sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m(C_5H_8O_4$, 298.15 K$) = (119.8 \pm 1.2)$ kJ mol^{-1} was obtained for glutaric acid. This is in excellent agreement with the value $\Delta_l^g H_m(C_5H_8O_4$, 298.15 K$) = (121.5 \pm 8)$ kJ mol^{-1}, obtained above (see also Table 14). For pimelic acid, the enthalpy of sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m(C_7H_{12}O_4$, 298.15 K$) = (139.9 \pm 1.0)$ kJ mol^{-1} was obtained by Ribeiro da Silva et al.,[80] which can

Table 16. Comparison of the Ideal-Gas Molar Enthalpies of Formation for Dicarboxylic Acids with Values Derived from Group Additivity[a,b]

dicarboxylic acid	$\Delta_f H^\circ_m$(g)/kJ·mol^{-1}	Σ group value	Δ
propanedioic acid	−779.7 ± 0.8	−781.6	1.9
butanedioic acid	−818.2 ± 3.3	−817.8	−0.4
pentanedioic acid	−839.0 ± 1.3	−838.0	−1.0
hexanedioic acid	−860.1 ± 1.5	−858.2	−1.9
heptanedioic acid	−877.2 ± 1.3	−878.5	1.3
octanedioic acid	−890.2 ± 4.1	−898.7	8.5
nonanedioic acid	−894.4 ± 2.6	−918.9	24.5
decanedioic acid	−917.3 ± 3.6	−939.1	21.8
undecanedioic acid	−936.9 ± 3.2	−959.3	22.4
dodecanedioic acid	−972.4 ± 4.4	−979.5	7.1

[a] Except for glutaric (pentanedioic) and pimelic (heptanedioic) acids, values for the ideal-gas enthalpies of formation are from Table 6 of Ribeiro da Silva et al.[80] [b] For glutaric and pimelic acids, values for the enthalpies of formation are derived by combining the crystalline enthalpies of formation given in Table 14 with the measured enthalpies of sublimation of Ribeiro da Silva et al.[80]

be compared with the value $\Delta_{cr}^{g}H_m(C_7H_{12}O_4$, 298.15 K) = 132.5 kJ mol^{-1}, derived above. Table 16 compares the ideal-gas enthalpies of formation for the dicarboxylic acids (propanedioic through dodecanedioic) with values derived using group additivity. From propanedioic through heptanedioic acids, the agreement is excellent. For the higher diacids, the agreement is not good. This may be due to possible cyclization of the higher acids in the gas phase. Both Ribeiro da Silva et al.[80] and, earlier, Davies and Thomas[81] suggested that the higher acids are partially cyclized by intramolecular interactions in the vapor phase. Further research including repeat measurements of the enthalpies of combustion of the higher diacids would help elucidate the situation.

Cyclohexanone Oxime. Thermodynamic property determinations on cyclohexanone oxime have been reported by Kozyro et al. in three papers.[74−76] Measurements included in the communications were energies of combustion, heat capacities for the liquid and solid phases, vapor pressures and sublimation pressures, and experimental determination of the enthalpies of fusion, vaporization, and sublimation. In addition, a previous determination of the enthalpy of combustion of cyclohexanone oxime was reported by Runge and Maass in 1953.[77]

The values for the enthalpy of combustion of solid cyclohexanone oxime found in the literature search were $\Delta_c H^\circ_m(C_6H_{11}NO$, cr, 298.15 K) = −(3723 ± 4) kJ·mol^{-1} by Runge and Maass,[77] $\Delta_c H^\circ_m(C_6H_{11}NO$, cr, 298.15 K) = −(3777.57 ± 3.75) kJ·mol^{-1} by Kozyro et al.,[74] and $\Delta_c H^\circ_m(C_6H_{11}NO$, cr, 298.15 K) = −(3779.94 ± 2.34) kJ·mol^{-1} by Kozyro et al.[76] Kozyro et al.[76] reference another determination of the enthalpy of combustion of cyclohexanone oxime by Lebedev et al.,[78] $\Delta_c H^\circ_m(C_6H_{11}NO$, cr, 298.15 K) = −(3785.7 ± 1.7) kJ·mol^{-1}. (All efforts by us to obtain a copy of that reference proved unsuccessful.) The Kozyro et al.,[74,76] values are both in good agreement with that obtained in this research: $\Delta_c H^\circ_m(C_6H_{11}NO$, cr, 298.15 K) = −(3780.41 ± 0.68) kJ·mol^{-1} (Table 6) based on carbon dioxide recovery.

The heat capacity values and equations representing the variation with temperature (see Table 8) obtained in this research are somewhat different from those obtained and reported by Kozyro et al.[75] However, the derived enthalpy of fusion and melting temperature are both in agreement with the Kozyro et al.[75] values.

Vapor-pressure measurements on cyclohexanone oxime using the inclined-piston apparatus are reported in Table 7. The reported values are approximately 5 to 10% less than corresponding values derived using the equations listed in refs 75 and 76. (Kozyro et al. used a Knudsen effusion technique for the sublimation-pressure measurements and a membrane null-manometer for measurements made above the fusion temperature.)

Enthalpies of sublimation, $\Delta_{cr}^{g}H_m$, and vaporization, $\Delta_{l}^{g}H_m$, at the respective mean temperatures were derived and are listed in Table 7. Enthalpies of sublimation and vaporization at 298.15 K were derived by combining those results with the heat-capacity measurements in Table 8. Values are listed in Table 13. In Table 14 the weighted mean value $\Delta_{cr}^{g}H_m(C_6H_{11}NO$, 298.15 K) = (79.6 ± 1.8) kJ·mol^{-1} is used in the derivation of the ideal-gas enthalpy of formation of cyclohexanone oxime. The enthalpies obtained in this research mirror values obtained using the direct calorimetric methods of Kozyro et al. and reported in their 1992 paper.[76] Corresponding values reported by Kozyro et al.,[76] obtained using their vapor-pressure data, were 4 to 5 kJ·mol^{-1} different (“well outside total measurement errors”).

Estimation of the ideal-gas enthalpy of formation of cyclohexanone oxime follows. Using group parameters derived within this project,

5	C−(C)$_2$(H)$_2$	−20.21×5=−101.05
	C−(C)$_2$(NOH)	???

$$\Delta_f H^\circ_m(C_6H_{11}NO, g, 298.15\ K) = -72.8\ kJ\cdot mol^{-1}$$

Hence the C−(C)$_2$(NOH) group-additivity parameter equals 28.3 kJ·mol^{-1}. Other ideal-gas standard enthalpies of formation of oximes are required to confirm this group-additivity parameter.

Conclusions: Confirmation of Literature Enthalpies of Formation, Revised Groups, and Interaction Terms

The measured enthalpy of formation of 1,4-diisopropylbenzene is in excellent agreement with the reaction calorimetric work of Popov et al.[49] Slight modification of the C−(C$_b$)(C)$_2$(H) group parameter from −4.1 kJ·mol^{-1} to −3.2 kJ·mol^{-1} is suggested.

Comments are made on the size of ortho interaction terms in benzene compounds, and a tentative value of 9.2 kJ·mol^{-1} is assigned to the isopropyl ortho interaction. Further work is required to elucidate the situation.

The recently published work of Verevkin,[59] who measured the thermochemical properties of 1,3-di-, 1,4-di-, and 1,3,5-triisopropylbenzenes, is in good agreement with the results obtained in this research.

A value of −1.2 kJ·mol^{-1} is assigned to the C−(CO)$_2$(H)$_2$ group parameter. A personal communication between Sergey Verevkin and an author (RDC) established that a compound listed in ref 62 as diethyl malonate was *not* that compound. Therefore, the results listed in ref 62 could not be used to confirm the new group parameter.

The energy of combustion of glutaric acid is confirmed and, in combination with literature vapor-pressure data, an enthalpy of formation for the ideal gas derived. Any errors in the group parameters used to estimate the ideal-gas enthalpies of formation of dicarboxylic acids are shown to be small. The results are used to derive an estimate for the enthalpy of sublimation of pimelic acid, namely, $\Delta_{cr}^{g}H_m(C_7H_{12}O_4$, 298.15 K) = 132.5 kJ mol^{-1}.

Subsequent to this research, the measurements of Ribeiro da Silva et al.[80] confirm the above conclusions for both acids.

Literature measurements on cyclohexanone oxime are shown to be compatible with those obtained here. A value of 28.3 kJ·mol^{-1} was derived for the C−(C)$_2$(NOH) group parameter in oximes.

In addition, values of the critical properties of three of the compounds were derived: $T_c = (675 \pm 1)$ K with $\rho_c = (263 \pm 10)$ kg·m^{-3} and $p_c = (2330 \pm 100)$ kPa for 1,4-diisopropylbenzene, $T_c = (703 \pm 2)$ K with $\rho_c = (270 \pm 30)$ kg·m^{-3} and $p_c = (1600 \pm 300)$ kPa for 1,2,4,5-tetraisopropylbenzene, and $T_c = (647 \pm 3)$ K with $\rho_c = (350 \pm 15)$ kg·m^{-3} and $p_c = (3600 \pm 300)$ kPa for dimethyl malonate, respectively.

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