Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for Butyl Vinyl Ether, 1,2-Dimethoxyethane, Methyl Glycolate, Bicyclo[2.2.1]hept-2-ene, 5-Vinylbicyclo[2.2.1]hept-2-ene, *trans*-Azobenzene, Butyl Acrylate, Di-*tert*-butyl Ether, and Hexane-1,6-diol

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Ideal-gas enthalpies of formation of butyl vinyl ether, 1,2-dimethoxyethane, methyl glycolate, bicyclo-[2.2.1]hept-2-ene, 5-vinylbicyclo[2.2.1]hept-2-ene, *trans*-azobenzene, butyl acrylate, di-*tert*-butyl ether, and hexane-1,6-diol are reported. Enthalpies of fusion were determined for bicyclo[2.2.1]hept-2-ene and *trans*-azobenzene. Two-phase (solid + vapor) or (liquid + vapor) heat capacities were determined from 300 K to the critical region or earlier decomposition temperature for each compound studied. Liquid-phase densities along the saturation line were measured for bicyclo[2.2.1]hept-2-ene. For butyl vinyl ether and 1,2-dimethoxyethane, critical temperatures and critical densities were determined from the dsc results and corresponding critical pressures derived from the fitting procedures. Fitting procedures were used to derive critical temperatures, critical pressures, and critical densities for bicyclo[2.2.1]hept-2-ene, 5-vinylbicyclo[2.2.1]hept-2-ene, *trans*-azobenzene, butyl acrylate, and di-*tert*-butyl ether. Group-additivity parameters or ring-correction terms useful in the application of the Benson group-contribution correlations were derived.

Introduction

This research was funded jointly by the U.S. Department of Energy (DOE) through the Office of Fossil Energy's Advanced Exploratory Research 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 work performed in the sixth year of this project (DIPPR Research Project 871: Determination of Pure Compound Ideal-Gas Enthalpies of Formation) represents the outcome of interactions between representatives of the DOE Bartlesville Project Office, DIPPR, and the National Institute for Petroleum and Energy Research (NIPER) staff.

Research programs funded by DOE Fossil Energy at NIPER share a common goal: the accurate estimation of both the thermochemical and thermophysical properties for a range of organic compounds, which are important in the processing of alternate fuel sources. Our research has shown that there are a number of key "small" organic compounds for which thermochemical and thermophysical properties are incomplete, in question, or just completely unknown. Data on these compounds will greatly enhance the application of group-contribution methodology (Benson, 1976; Reid et al., 1987) as a property-estimation tool.

In the 1992 project year, nine compounds were chosen for experimental studies. For one of the compounds, hexane-1,6-diol, inclined-piston vapor pressure measurements were made to supplement the work reported in the 1989 project (Steele et al., 1991b) in an attempt to resolve problems with the earlier results (Steele et al., 1991b, 1994b). The molecular structures, Chemical Abstracts Service (CAS) names, commonly used trivial names, and CAS Registry Numbers of the compounds studied, are

shown in Figure 1. 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 required auxiliary measurements for each of the compounds is given in Table 1.

Experimental Section

In this section, details are given of the apparatus and procedures used in the reported measurements. These have been previously described in the literature and in various DOE reports. Therefore, details have been kept to a minimum here and the literature referenced for further consultation.

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 calorimetric measurements. All compounds except di-*tert*-butyl ether were purchased from Aldrich Chemical Co. Capillary gas chromatography (cgc) analyses on the purchased samples gave an average purity of 99.8 mol %. Di-*tert*-butyl ether was obtained from one of the project sponsors with a purity of 99.9 mol %. Only sufficient sample for combustion measurements was available. All the other compounds were purified by J. Reynolds of the NIPER Analytical Chemistry Group. Repeated spinning-band distillations were used to purify the compounds. Cgc 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 the small differences between the boiling and condensation temperatures in the ebulliometric vapor-pressure measurements, reported in this paper.

All transfers of the samples were made under nitrogen or helium or by vacuum distillation. The water used as a

Bicyclo[2,2,1]hept-2-ene
Norbornene
[498-66-8]

CH$_2$=CH

Bicyclo[2,2,1]hept-2-ene, 5-vinyl-
5-Vinylnorbornene
[3048-64-4]

N=N

(E)-Diazene, diphenyl-
***trans*-Azobenzene**
[17082-12-1]

HO(CH$_2$)$_6$OH

1,6-Hexanediol
Hexa-1,6-diol
[629-11-8]

CH$_2$=CHO(CH$_2$)$_3$CH$_3$

Butane, 1-(ethenyloxy)-
Ether, butyl vinyl
Butyl vinyl ether
[111-34-2]

CH$_2$=CHCO$_2$(CH$_2$)$_3$CH$_3$

2-Propenoic acid butyl ester
Acrylic acid, butyl ester
Butyl acrylate
[141-32-2]

(CH$_3$)$_3$COC(CH$_3$)$_3$

Propane, 2,2'-oxybis[2-methyl-
***tert*-butyl ether**
Di-*tert*-butyl ether
[6163-66-2]

CH$_3$OCH$_2$CH$_2$OCH$_3$

Ethane, 1,2-dimethoxy-
1,2-Dimethoxyethane
Ethylene glycol dimethyl ether
[110-71-4]

HOCH$_2$CO$_2$CH$_3$

Acetic acid, hydroxy-, methyl ester
Glycolic acid, methyl ester
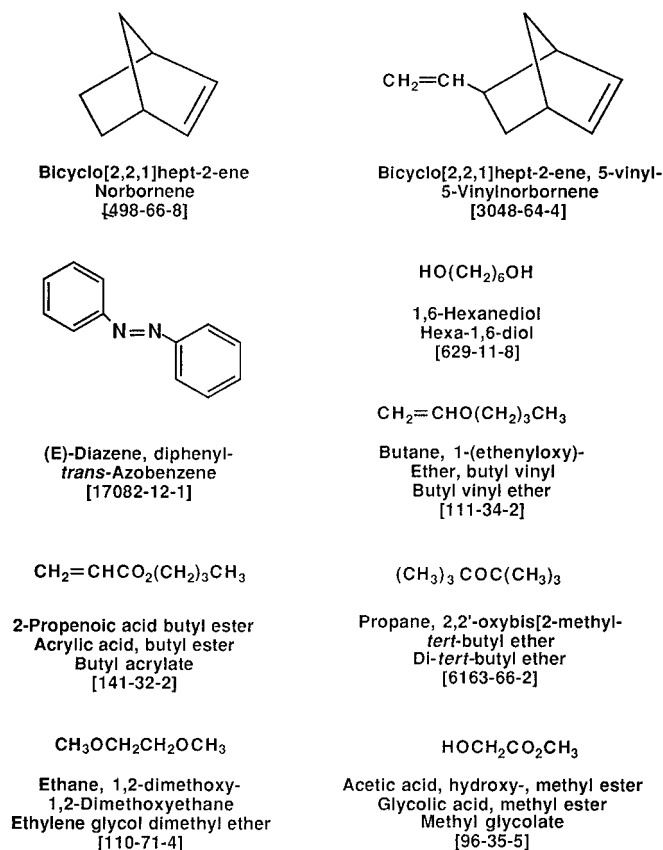**Methyl glycolate**
[96-35-5]

Figure 1. Molecular structures, Chemical Abstracts Service names (provided by the authors), commonly used trivial names, and CAS Registry Numbers (provided by the authors) for the compounds studied in this research.

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

compound	$\Delta_c U_m^o$	vapor pressure	heat capacity
butyl vinyl ether	x	x	x
1,2-dimethoxyethane	x	x	x
methyl glycolate	x	x	x
bicyclo[2.2.1]hept-2-ene	x	x	x
5-vinylbicyclo[2.2.1]hept-2-ene	x	x	x
trans-azobenzene	x	x	x
butyl acrylate	x	x	x
di-*tert*-butyl ether	x		
hexane-1,6-diol		x	

[a] Measurements made are denoted by x. [b] In addition, liquid-phase density measurements along the saturation line in the temperature range 323 K to 423 K were made for bicyclo[2.2.1]hept-2-ene, and the critical temperature, pressure, and density were derived. For butyl vinyl ether, and 1,2-dimethoxyethane critical temperatures and critical densities were determined from the dsc measurements. Values for the critical temperature and critical pressure for 5-vinylbicyclo[2.2.1]hept-2-ene, *trans*-azobenzene, butyl acrylate, and di-*tert*-butyl ether were also derived using the fitting procedures.

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. Cgc 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 (IUPAC, 1993) and the gas constant, $R = 8.314\,51$ J·K^{-1}·mol^{-1}, adopted

by CODATA (Cohen and Taylor, 1988). The platinum resistance thermometers used in these measurements were calibrated by comparison with standard thermometers whose constants were determined at the National Institute for Standards and Technology (NIST). All temperatures are reported in terms of ITS-90 (Goldberg and Weir, 1990; Mangum and Furukawa, 1990). 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 National Institute for Petroleum and Energy Research have been described by Good (1969, 1972), Good and Smith (1969), and Steele et al. (1988a). A rotating-bomb calorimeter (laboratory designation BMR II) (Good et al., 1956) and a platinum-lined bomb (laboratory designation Pt-3b) (Good et al., 1959) with an internal volume of 0.3934 dm^3 were used with rotation in the first series of combustions and without rotation in the remaining series. Flexible borosilicate-glass ampules (Guthrie et al., 1952; Good, 1972) were used to confine the samples which were liquid at 298 K. Bicyclo[2.2.1]hept-2-ene was burned in pellet form enclosed in two polyester film bags (Good et al., 1956). All experiments 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 $-(26\,434.0 \pm 3.0)$ J·g^{-1} under certificate conditions. Conversion to standard states (Hubbard et al., 1956) gives $-(26\,413.7 \pm 3.0)$ J·g^{-1} for $\Delta_c U_m^o/M$, the standard specific energy of the idealized combustion reaction. The combustion measurements were performed in four separate series over a nine month period as the purified compounds became available. Calibration experiments were interspersed with each series of measurements. Nitrogen oxides were not formed in the calibration experiments due to the high purity of the oxygen used and preliminary bomb flushing.

In the first combustion series the energy equivalent of the calorimeter, ϵ(calor), obtained was $(16\,769.3 \pm 0.5)$ J·K^{-1} (mean and standard deviation of the mean) for the butyl vinyl ether measurements. In the second combustion series ϵ(calor) was $(16\,768.3 \pm 0.8)$ J·K^{-1} for the 1,2-dimethoxyethane and methyl glycolate measurements. The temperature rise was only 1.5 K and not the usual 2 K. This was necessitated by the low energy of combustion of methyl glycolate. In trial experiments, combustion of sufficient sample to obtain a 2 K temperature rise invariably resulted in an explosion within the bomb and the formation of large amounts of soot. In the third series the energy equivalent of the calorimeter, ϵ(calor), obtained was $(16\,772.7 \pm 0.5)$ J·K^{-1} for the bicyclo[2.2.1]hept-2-ene, 5-vinylbicyclo[2.2.1]hept-2-ene, *trans*-azobenzene, and butyl acrylate measurements. Finally, in the fourth series ϵ(calor) was $(16\,772.2 \pm 0.4)$ J·K^{-1} for the di-*tert*-butyl ether combustions. The changes in the energy equivalent represented small repairs to the bomb to cure leaking gaskets which develop with age and continual usage. (The bomb calorimeter Pt-3b is now over 40 years old!)

The auxiliary oil (laboratory designation TKL66) had the empirical formula CH$_{1.913}$. For this material, $\Delta_c U_m^o/M$ was $-(46\,042.5 \pm 1.8)$ J·g^{-1} (mean and standard deviation). For the cotton fuse, empirical formula CH$_{1.774}$O$_{0.887}$, $\Delta_c U_m^o/M$ was $-16\,945$ J·g^{-1}.

The value for $\Delta_c U_m^o/M$ obtained for the polyester film, empirical formula C$_{10}$H$_8$O$_4$, was a function of the relative

Table 2. Physical Properties at 298.15 K[a]

compound	ρ/kg·m^{-3}	$10^7(\partial V/\partial T)_p$/ m^3·K^{-1}	C_p/R
butyl vinyl ether	769.0	1.65	26.7
1,2-dimethoxyethane	862.0	1.34	23.3
methyl glycolate	1167	1.5	23.6
bicyclo[2.2.1]hept-2-ene[b]	900.0	(0.3)	15.9
5-vinylbicyclo[2.2.1]hept-2-ene	884.3	1.35	24.25
trans-azobenzene[b]	1217	(0.3)	27.5
butyl acrylate	893.2	1.34	28.75
di-*tert*-butyl ether	757.7	1.59	(33.2)

[a] Values in parentheses are estimates. [b] Solid, all other compounds are in the liquid phase.

Table 3. Carbon Dioxide Recoveries

compound	no. of expts	% recovery[a]
benzoic acid calibration	7	99.999 ± 0.005
butyl vinyl ether	6	100.013 ± 0.016
benzoic acid calibration	8	100.001 ± 0.002
1,2-dimethoxyethane	5	99.995 ± 0.009
methyl glycolate	6	99.999 ± 0.004
benzoic acid calibration	9	100.012 ± 0.007
bicyclo[2.2.1]hept-2-ene	6	99.730 ± 0.086[b]
5-vinylbicyclo[2.2.1]hept-2-ene	6	100.019 ± 0.017
trans-azobenzene	6	100.012 ± 0.014
butyl acrylate	5	100.018 ± 0.014
benzoic acid calibration	6	100.011 ± 0.007
di-*tert*-butyl ether	5	99.995 ± 0.009

[a] Mean and standard deviation of the mean. [b] Results of combustion study based on percentage CO_2 recovery (see text).

humidity (RH) in the laboratory during weightings (Good et al., 1956):

$$\{(\Delta_c U_m^o/M)/J\cdot g^{-1}\} = -22912.0 - 1.0560(\text{RH}) \quad (1)$$

Information necessary for reducing apparent mass measured in air to mass, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states (Hubbard et al., 1956) is given in Table 2.

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, or from the dimensions of a pellet of known mass for the compounds which were solid at 298.15 K (*trans*-azobenzene and bicyclo[2.2.1]hept-2-ene). Values of the heat capacity of each sample at 298.15 K were measured using a differential scanning calorimeter as described later.

Nitric acid, formed during combustions of the *trans*-azobenzene, was determined by titration with standard sodium hydroxide (Good and Moore, 1970). Carbon dioxide was also recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as adsorbent for the CO_2 recoveries (Good and Smith, 1969). 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 calibration series and the corresponding compound energy determinations are listed in Table 3.

Vapor-Pressure Apparatus and Procedures. The essential features of the ebulliometric equipment and procedures for vapor-pressure measurements are described in the literature (Swietoslawski, 1945; Osborn and Douslin, 1966; Chirico et al., 1989b). The ebulliometers were used to reflux the substance under study with a standard of known vapor pressure under a common helium atmosphere. In the pressure region 25 kPa to 270 kPa, water was used as the standard, and the pressures were derived using the internationally accepted equation of state for

ordinary water revised to ITS-90 (Wagner and Pruss, 1993). In the pressure region 2 kPa to 25 kPa, decane (Chirico et al., 1989b) was used as the standard. Pressures were calculated on ITS-90 for those measurements using the equation:

$$\ln(p/\text{kPa}) = 7.73165 + (1/T_r)\{-9.98917(1 - T_r) + 5.28411(1 - T_r)^{1.5} - 6.51326(1 - T_r)^{2.5} - 2.68400(1 - T_r)^5\} \quad (2)$$

where $T_r = T/(617.650 \text{ K})$ and T denotes the condensation temperature for the decane.

The precision in the temperature measurements for the ebulliometric vapor-pressure studies was 0.001 K. Uncertainties in the pressures are adequately described by

$$\sigma(p) = (0.001)\{(dp_{ref}/dT)^2 + (dp_x/dT)^2\}^{1/2} \quad (3)$$

where p_{ref} is the vapor pressure of the reference substance and p_x is the vapor pressure of the sample under study.

The equipment for the inclined-piston vapor-pressure measurements has been described by Douslin and Mc-Cullough (1963) and Douslin and Osborn (1965). Recent revisions to the equipment and procedures have been reported (Steele et al., 1988a). The low pressure range of the inclined-piston measurements, 10 Pa to 3500 Pa, necessitated diligent outgassing of the sample prior to introduction into the apparatus. Also, prior to the sample introduction, all parts of the cell in contact with the sample were baked at 623 K under high vacuum (<10^{-4} Pa). The thoroughly outgassed sample was placed in the apparatus, and additional outgassing was performed prior to commencing measurements. Finally, prior to each measurement, a small amount of sample was pumped off. Measurements were made as a function of time to extrapolate the pressure to the time when the pumping valve was closed (i.e., to the time when insignificant amounts of light gas had leaked into the system or diffused out of the sample).

Uncertainties in the pressures determined with the inclined-piston apparatus, on the basis of estimated precision of measuring the mass, area, and angle of inclination of the piston, are adequately described by the expression

$$\sigma(p) = 1.5 \times 10^{-4}p + 0.2 \text{ Pa} \quad (4)$$

The uncertainties in the temperatures are 0.001 K. The contributions of the temperature uncertainties to $\sigma(p)$ are insignificant in the range of the measurements.

Differential Scanning Calorimetry. The technique and methodology used in the differential scanning calorimetric (dsc) measurements have been outlined in Steele et al. (1988b, 1994a), Chirico et al. (1989a), Knipmeyer et al. (1989), Chirico and Steele (1994), and Steele (1995). The major difference between our measurement technique and that used by Mraw and Naas (1979) is the substitution of specially designed cells (Steele et al., 1988a) for the aluminum "volatile sample cells". These cells, designed and manufactured at NIPER, are made of 17-4 PH stainless steel and can withstand both high pressures (to 7.6 MPa) and high temperatures (to 900 K). The theoretical background for the determination of heat capacities at vapor-saturation pressure, $C_{sat,m}$, from $C_{x,m}^{II}$ values obtained with a dsc has been described (Steele et al., 1988b, 1994a; Chirico et al., 1989a; Knipmeyer et al., 1989; Chirico and Steele, 1994; Steele, 1995). The review (Steele, 1995) is detailed and will be repeatedly referenced throughout the rest of this paper.

Table 4. Typical Combustion Experiments at 298.15 K for C, H, N, O Compounds ($p° = 101.325$ kPa)[a,b]

	A	B	C	D	E	F	G	H
m'(compound)/g	0.859 176	0.742 701	1.106 327	0.718 061	0.667 066	0.947 189	0.814 964	0.734 675
m''(oil)/g	0.076 898	0.078 619	0.168 045		0.081 842	0.171 052	0.079 126	
m'''(fuse)/g	0.001 964	0.001 956	0.001 659	0.002 692	0.001 136	0.001 413	0.001 129	0.001 926
m''''(polyester)/g				0.084 064				
n_i(H$_2$O)/mol	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35
m(Pt)/g	19.969	19.969	32.477	32.473	32.490	19.982	32.488	19.984
ΔT/K[c]	2.182 50	1.504 41	1.508 74	2.037 09	1.999 79	2.006 35	2.001 43	2.004 65
ϵ(calor)(ΔT)/J	−36 598.9	−25 227.3	−25 316.6	−34 167.4	−33 540.7	−33 651.9	−33 569.4	−33 602.4
ϵ(cont)(ΔT)/J[d]	−42.4	−28.8	−32.9	−40.3	−39.7	−36.5	−40.6	−40.7
ΔU_{ign}/J	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
ΔU(corr std states)/J[e]	13.5	9.2	17.2	15.0	13.9	20.4	15.1	19.1
ΔU_{dec}(HNO$_3$)/J						71.8		
$−m''(\Delta_c U_m^o/M)$(oil)/J	3540.6	3619.8	7737.2		3768.2		7875.6	3643.2
$−m'''(\Delta_c U_m^o/M)$(fuse)/J	33.3	33.1	28.1	44.6	19.2	23.9	19.1	32.6
$−m''''(\Delta_c U_m^o/M)$(polyester)/J				1919.7				
$m(\Delta_c U_m^o/M)$(compound)/J	−33 053.1	−21 593.2	−17 566.2	−32 227.6	−29 779.3	−33 571.5	−25 699.4	−29 967.4
$(\Delta_c U_m^o/M)$(compound)/J·g^{-1}	−38 470.6	−29 076.9	−15 878.0	−44 881.5	−44 642.2	−35 443.2	−31 534.4	−40 790.0

[a] A = butyl vinyl ether, B = 1,2-dimethoxyethane, C = methyl glycolate, D = bicyclo[2.2.1]hept-2-ene, E = 5-vinylbicyclo[2.2.1]hept-2-ene, F = *trans*-azobenzene, G = butyl acrylate, and H = di-*tert*-butyl ether. [b] The symbols and abbreviations of this table are those of Hubbard et al. (1956) except as noted. [c] ΔT/K = $(T_i − T_f + \Delta T_{corr})$/K. [d] ϵ_i(cont)$(T_i − 298.15$ K$) + \epsilon_f$(cont)$(298.15$ K $− T_f + \Delta T_{corr})$. [e] Items 81–85, 87–90, 93, and 94 of the computational form of Hubbard et al. (1956).

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

Butyl Vinyl Ether
$\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g^{-1}
−38 470.6, −38 466.6, −38 498.3
−38 487.6, −38 469.7, −38 474.5

$\langle\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g$^{-1}\rangle$ −38 477.9 ± 5.1

1,2-Dimethoxyethane
$\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g^{-1}
−29 076.9, −29 070.4, −29 067.6
−29 066.4, −29 066.0

$\langle\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g$^{-1}\rangle$ −29 070.5 ± 2.4

Methyl Glycolate
$\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g^{-1}
−15 878.0, −15 852.8, −15 848.7
−15 855.0, −15 871.7, −15 850.3

$\langle\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g$^{-1}\rangle$ −15 859.4 ± 5.0

Bicyclo[2.2.1]hept-2-ene
$\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g^{-1}
−44 881.5, −44 825.5, −44 823.7
−44 857.8, −44 827.2, −44 821.8

$\langle\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g$^{-1}\rangle$ −44 839.6 ± 10.0

5-Vinylbicyclo[2.2.1]hept-2-ene
$\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g^{-1}
−44 642.2, −44 638.4, −44 644.7
−44 641.2, −44 641.8, −44 637.9

$\langle\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g$^{-1}\rangle$ −44 641.0 ± 1.0

trans-Azobenzene
$\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g^{-1}
−35 443.2, −35 444.4, −35 446.8
−35 446.8, −35 444.0, −35 444.1

$\langle\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g$^{-1}\rangle$ −35 444.9 ± 0.8

Butyl Acrylate
$\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g^{-1}
−31 534.4, −31 533.3, −31 536.6
−31 537.2, −31 537.5

$\langle\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g$^{-1}\rangle$ −31 535.8 ± 0.8

Di-*tert*-butyl Ether
$\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g^{-1}
−40 790.0, −40 789.5, −40 788.5
−40 792.4, −40 791.2

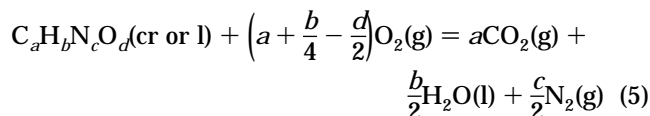$\langle\{(\Delta_c U_m^o/M)$(compound)$\}$/J·g$^{-1}\rangle$ −40 790.3 ± 0.7

[a] The uncertainties shown are one standard deviation of the mean.

Densitometry. Densities, ρ, at saturation pressure for the liquid phase for a range of temperatures were obtained in this research with a vibrating-tube densitometer. The densitometer design is essentially that used successfully by Dr. J. M. Simonson and his colleagues at Oak Ridge National Laboratory for the study of aqueous salt mixtures at high temperatures and pressures (Simonson et al., 1994). The instrument and its operation have been described (Chirico et al., 1993). Test measurements of the density of benzene between $T = 310$ K and $T = 523$ K have been reported (Chirico and Steele, 1994). Results agreed with the values published by (Hales and Townsend, 1972) within $1 \times 10^{-3}\rho$. The precision of the measurements was approximately $5 \times 10^{-4}\rho$.
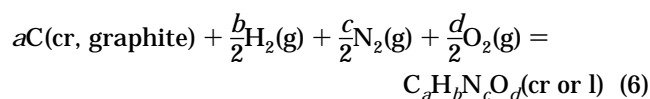
Results

Combustion Calorimetry. A typical combustion experiment for each compound studied is summarized in Table 4. It is impractical to list summaries for each combustion, but values of $\Delta_c U_m^o/M$ for all the experiments are reported in Table 5. Values of $\Delta_c U_m^o/M$ in Tables 4 and 5 for the C, H, N, O compounds refer to the general reaction

$$C_aH_bN_cO_d(\text{cr or l}) + \left(a + \frac{b}{4} - \frac{d}{2}\right)O_2(g) = aCO_2(g) + \frac{b}{2}H_2O(l) + \frac{c}{2}N_2(g) \quad (5)$$

Corrections for the small amounts of nitric acid, formed during combustions of *trans*-azobenzene, were made during the conversion to standard states (Hubbard et al., 1956) 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$_2$O (l).

For bicyclo[2.2.1]hept-2-ene the values of $\Delta_c U_m^o/M$ refer to the unit mass of sample derived from the corresponding carbon dioxide analyses of the combustion products (see Table 3). Table 6 gives derived values of the standard molar energy of combustion $\Delta_c U_m^o$, the standard molar enthalpy of combustion $\Delta_c H_m^o$, and the standard molar enthalpy of formation $\Delta_f H_m^o$, for the compounds studied. Values of $\Delta_c U_m^o$ and $\Delta_c H_m^o$ for the C, H, N, O compounds refer to eq 5. The corresponding values of $\Delta_f H_m^o$ refer to the reaction

$$aC(\text{cr, graphite}) + \frac{b}{2}H_2(g) + \frac{c}{2}N_2(g) + \frac{d}{2}O_2(g) = C_aH_bN_cO_d(\text{cr or l}) \quad (6)$$

Uncertainties given in Table 6 are the "uncertainty interval" (Rossini, 1956). The enthalpies of formation of CO$_2$-

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

	$\Delta_c U_m^\circ$/kJ·mol^{-1}	$\Delta_c H_m^\circ$/kJ·mol^{-1}	$\Delta_f H_m^\circ$/kJ·mol^{-1}
A	-3854.00 ± 1.12	-3860.20 ± 1.12	-215.84 ± 1.18
B	-2619.91 ± 0.58	-2623.63 ± 0.58	-379.56 ± 0.64
C	-1428.61 ± 0.94	-1428.61 ± 0.94	-609.41 ± 0.94
D	-4221.96 ± 1.96	-4228.16 ± 1.96	44.44 ± 2.00
E	-5365.63 ± 0.74	-5373.07 ± 0.74	116.50 ± 0.88
F	-6458.96 ± 0.88	-6462.68 ± 0.88	311.41 ± 1.04
G	-4042.00 ± 0.58	-4046.96 ± 0.58	-422.59 ± 0.70
H	-5312.18 ± 0.61	-5322.10 ± 0.61	-398.45 ± 0.72

[a] A = butyl vinyl ether, B = 1,2-dimethoxyethane, C = methyl glycolate, D = bicyclo[2.2.1]hept-2-ene, E = 5-vinylbicyclo[2.2.1]hept-2-ene, F = *trans*-azobenzene, G = butyl acrylate, and H = di-*tert*-butyl ether. [b] The results listed in this table are for the stable condensed phase at 298.15 K: for bicyclo[2.2.1]hept-2-ene and *trans*-azobenzene the crystalline phase (c1), and the liquid phase for each of the other compounds.

(g) and H_2O(l) were taken to be $-(393.51 \pm 0.13)$ and $-(285.830 \pm 0.042)$ kJ·mol^{-1}, respectively, as assigned by CODATA (Cox et al., 1989).

Vapor-Pressure Measurements. Measured vapor pressures for each of the compounds are listed in Table 7. The results for di-*tert*-butyl ether are those of Ambrose et al. (1976) obtained using an ebulliometer, converted to ITS-90. The precision in the temperature measurements was given by Ambrose et al. (1976) as ±0.003 K. Following previous practice (Osborn and Douslin, 1966; Chirico et al., 1989b), the results obtained in the NIPER ebulliometric measurements were adjusted to common pressures. The common pressures, the condensation temperatures, and the difference between the condensation and boiling temperatures for the samples 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.

Inclined-piston vapor-pressure measurements for hexane-1,6-diol are also listed in Table 7. For hexane-1,6-diol, the inclined-piston values extend the range of measured values down by an additional 67 K from those reported previously (Steele et al., 1991b).

The difference between the boiling and condensation temperatures (ΔT) for 5-vinylbicyclo[2.2.1]hept-2-ene increased significantly above 425 K. An attempt was made to make a measurement at 143.25 kPa (427.5 K), but ΔT started at approximately 0.04 K and rapidly increased to 0.25 K. This phenomenon is normally indicative of sample decomposition. For butyl acrylate at 426 K the sample became very viscous, which was indicative of polymerization. The methyl glycolate sample was also sensitive to heat and rapidly decomposed at approximately 387 K, hence, the narrow range of vapor pressure measurements, 326 K to 381 K, 2 kPa to 25 kPa, obtained (see Table 7).

Differential Scanning Calorimetry. Table 8 lists the two-phase (liquid + vapor) heat capacities $C_{x,m}^{II}$ determined by dsc for butyl vinyl ether, 1,2-dimethoxyethane, bicyclo[2.2.1]hept-2-ene, 5-vinylbicyclo[2.2.1]hept-2-ene, methyl glycolate, *trans*-azobenzene, and butyl acrylate for the given 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 heats. For each compound the upper temperature bound of the measurements was set by the critical region or earlier sample decomposition.

For butyl vinyl ether and 1,2-dimethoxyethane, measurements in the critical region were possible. For each compound an abrupt decrease in the heat capacity associated with the conversion from two phases to one phase was observed (see Table 8). In each case, sample decomposition was greatly reduced by employing a single continuous heat

at a heating rate of 0.333 K·s^{-1}. Temperatures at which conversion to the single phase occurred were obtained from those measurements. Table 9 reports the density, obtained from the mass of sample and the cell volume calculated with eq 7, and the measured temperatures at which conversion to a single phase was observed.

In this research, the thermal expansion of the cells was expressed as

$$V_x(T)/V_x(298.15\ \text{K}) = 1 + ay + by^2 \qquad (7)$$

where $y = (T - 298.15)$ K, $a = 3.216 \times 10^{-5}$ K^{-1}, and $b = 5.4 \times 10^{-8}$ K^{-2}.

Critical temperatures and critical densities were derived graphically for butyl vinyl ether and 1,2-dimethoxyethane with these results, as seen in Figure 2. Results of measurements on benzene and toluene performed as "proof-of-concept measurements" for these procedures have been reported (Knipmeyer et al., 1989). The rapid heating method was used previously for critical temperature and critical density determinations for 2-aminobiphenyl (Steele et al., 1991a), dibenzothiophene (Chirico et al., 1991), carbazole, phenanthrene, and benzofuran (Steele, 1995).

For the compounds which were solid at 298.15 K, bicyclo[2.2.1]hept-2-ene and *trans*-azobenzene, by judicious choice of starting temperature, the melting endotherms 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. Figure 3 shows the thermochemical cycle used to "correct" the enthalpy of fusion of the compound at its melting point to the corresponding value at the standard temperature of 298.15 K. Details of the derived enthalpies of fusion for both bicyclo[2.2.1]hept-2-ene and *trans*-azobenzene at their melting points and the corresponding values at 298.15 K are reported in Table 8. Equations (representing the heat capacities for both the liquid and solid phases for each compound) which were used in the "correction" to 298.15 K are also reported in Table 8. [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.]

Densitometry. Measured densities for bicyclo[2.2.1]hept-2-ene in the liquid phase along the saturation line are listed in Table 10. The temperatures are precise to ±0.005 K.

Fitting Procedures. General Comments. 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 $\Delta_l^g H_m$ at 298.15 K is the only value necessary to obtain $\Delta_f H_m^\circ$(g, 298.15 K), the benefit of a knowledge of the enthalpy of vaporization over a wide range of temperature was recognized. The exact fitting procedure used for each compound varied depending on the range of measured properties available.

Bicyclo[2.2.1]hept-2-ene. For bicyclo[2.2.1]hept-2-ene the fitting parameters were derived by a simultaneous nonlinear least-squares fit of the vapor pressures listed in Table 7 and the two-phase heat capacities $C_{x,m}^{II}$ given in Table 8. The critical temperature, critical density, and the critical pressure p_c were included in the variables. A summary of the procedure follows.

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

method	T/K	p/kPa	Δp/kPa	ρ/kPa	ΔT/K	method	T/K	p/kPa	Δp/kPa	ρ/kPa	ΔT/K
					Butyl Vinyl Ether						
d	311.888	13.332	−0.002	0.001	0.027	w	355.394	70.120	−0.011	0.003	0.016
d	316.979	16.665	0.001	0.001	0.020	w	361.240	84.533	−0.006	0.004	0.016
d	321.216	19.933	0.001	0.001	0.020	w	367.131	101.325	−0.005	0.004	0.015
d	326.811	25.023	−0.008	0.001	0.018	w	373.062	120.79	0.01	0.00	0.018
w	326.795[b]	25.023	0.008	0.001	0.017	w	379.041	143.25	0.01	0.01	0.019
w	332.429	31.177	0.005	0.002	0.018	w	385.059	169.02	0.01	0.01	0.018
w	338.103	38.565	0.005	0.002	0.018	w	391.124	198.49	0.01	0.01	0.019
w	343.821	47.375	0.004	0.002	0.016	w	397.227	232.02	0.00	0.01	0.021
w	349.591	57.817	−0.013	0.003	0.016	w	403.373	270.02	−0.02	0.01	0.021
					1,2-Dimethoxyethane						
d	305.861	13.332	0.001	0.001	0.009	w	347.070	70.120	0.000	0.003	0.011
d	310.704	16.665	−0.001	0.001	0.008	w	352.591	84.533	0.000	0.004	0.011
d	314.727	19.933	−0.001	0.001	0.008	w	358.149	101.325	0.000	0.004	0.011
d	320.025	25.023	0.000	0.001	0.008	w	363.745	120.79	0.00	0.005	0.011
w	320.024[b]	25.023	0.001	0.001	0.008	w	369.380	143.25	0.00	0.01	0.011
w	325.360	31.177	0.001	0.002	0.008	w	375.049	169.02	0.00	0.01	0.012
w	330.733	38.565	−0.001	0.002	0.008	w	380.759	198.49	0.00	0.01	0.013
w	336.141	47.375	0.000	0.002	0.009	w	386.504	232.02	0.00	0.01	0.013
w	341.586	57.817	0.001	0.003	0.011	w	392.286	270.02	0.00	0.01	0.012
					Bicyclo[2.2.1]hept-2-ene						
w	338.655	38.568	0.003	0.002	0.009	w	375.011	120.76	0.01	0.01	0.014
w	344.592	47.372	−0.002	0.003	0.010	w	381.268	143.26	0.00	0.01	0.014
w	350.588	57.828	−0.006	0.003	0.010	w	387.559	169.03	0.00	0.01	0.014
w	356.610	70.106	−0.003	0.004	0.011	w	393.904	198.48	−0.02	0.01	0.013
w	362.701	84.534	0.001	0.004	0.012	w	400.301	232.01	−0.01	0.01	0.014
w	368.829	101.311	0.008	0.005	0.013	w	406.752	270.04	0.02	0.01	0.013
					5-Vinylbicyclo[2.2.1]hept-2-ene						
d	313.978	2.6660	0.0000	0.0002	0.014	w	367.405[b]	25.023	0.002	0.001	0.009
d	322.252	3.9999	0.0000	0.0003	0.011	w	373.886	31.177	0.000	0.002	0.008
d	328.446	5.3330	−0.0001	0.0003	0.011	w	380.417	38.565	0.001	0.002	0.011
d	337.680	7.9989	0.0002	0.0005	0.010	w	387.004	47.375	−0.001	0.002	0.011
d	344.628	10.666	−0.001	0.001	0.010	w	393.645	57.817	−0.004	0.003	0.013
d	350.255	13.332	0.000	0.001	0.009	w	407.093	84.533	−0.012	0.004	0.018
d	356.110	16.665	0.000	0.001	0.009	w	413.891	101.325	0.002	0.005	0.027
d	360.983	19.933	0.000	0.001	0.009	w	420.740[b]	120.790	0.034	0.005	0.039
d	367.405	25.023	0.002	0.001	0.009						
					trans-Azobenzene						
d	436.083	2.0014	0.0000	0.0001	0.063	w	530.136	38.559	0.002	0.002	0.015
d	443.377	2.6619	0.0000	0.0002	0.041	w	538.629	47.365	−0.002	0.002	0.012
d	454.304	3.9965	0.0000	0.0002	0.034	w	547.160	57.787	−0.001	0.003	0.013
d	462.480	5.3342	0.0000	0.0003	0.032	w	555.781	70.124	0.002	0.003	0.013
d	474.576	7.9964	−0.0001	0.0004	0.023	w	564.423	84.522	−0.001	0.004	0.011
d	483.619	10.650	0.000	0.001	0.021	w	573.125	101.319	0.000	0.004	0.012
d	490.956	13.309	0.000	0.001	0.020	w	581.876	120.78	0.00	0.00	0.013
d	498.592	16.642	0.000	0.001	0.018	w	590.683	143.25	0.00	0.01	0.015
d	504.929	19.908	0.000	0.001	0.017	w	599.528	169.04	0.00	0.01	0.017
d	513.345	25.045	0.000	0.001	0.016	w	608.407	198.46	0.01	0.01	0.024
w	513.290[b]	25.010	0.001	0.001	0.016	w	617.341	231.97	0.00	0.01	0.035
w	521.709	31.184	0.001	0.002	0.015	w	626.317	269.96	−0.01	0.01	0.055
					Butyl Acrylate						
d	318.513	2.0000	0.0003	0.0001	0.032	d	375.405	25.023	0.001	0.001	0.015
d	323.914	2.6660	−0.0002	0.0002	0.027	w	375.403[b]	25.023	0.003	0.001	0.015
d	331.929	3.9999	−0.0003	0.0003	0.023	w	381.611	31.177	0.001	0.002	0.014
d	337.919	5.3330	−0.0006	0.0003	0.020	w	387.862	38.565	−0.001	0.002	0.015
d	346.831	7.9989	−0.0001	0.0005	0.019	w	394.157	47.375	−0.004	0.002	0.015
d	353.523	10.666	0.000	0.001	0.017	w	400.495	57.817	−0.005	0.003	0.017
d	358.938	13.332	0.001	0.001	0.016	w	406.878	70.120	−0.005	0.003	0.018
d	364.565	16.665	0.001	0.001	0.016	w	413.303	84.533	0.000	0.004	0.020
d	369.243	19.933	0.001	0.001	0.016	w	419.771	101.325	0.010	0.005	0.024
					Di-*tert*-butyl Ether[c]						
A	289.866	2.913	−0.0007	0.0002		A	334.044	22.041	−0.017	0.001	
A	292.019	3.277	0.0053	0.0002		A	338.466	26.070	−0.018	0.001	
A	294.814	3.788	−0.0034	0.0003		A	343.537	31.389	−0.031	0.002	
A	298.558	4.592	−0.0033	0.0003		A	348.497	37.421	−0.028	0.002	
A	301.846	5.411	−0.0042	0.0004		A	353.748	44.772	−0.033	0.002	
A	305.669	6.512	−0.0073	0.0004		A	359.484	54.176	0.072	0.002	
A	309.188	7.689	−0.0069	0.0005		A	364.537	63.576	0.075	0.003	
A	313.091	9.197	−0.0055	0.0006		A	369.928	74.943	0.051	0.003	
A	316.902	10.986	0.0842	0.0006		A	375.792	89.022	−0.007	0.004	
A	320.901	12.945	−0.010	0.001		A	380.279	101.159	−0.019	0.004	
A	324.976	15.349	−0.016	0.001		A	381.226	103.830	−0.068	0.004	
A	328.886	18.000	−0.011	0.001		A	386.476	119.747	−0.267	0.004	

Table 7 (Continued)

method	T/K	p/kPa	Δp/kPa	ρ/kPa	ΔT/K	method	T/K	p/kPa	Δp/kPa	ρ/kPa	ΔT/K
						Hexane-1,6-diol[d]					
ip	354.976	0.0227	0.0001	0.0002		d	469.702	16.665	−0.001	0.001	0.018
ip	364.978	0.0515	0.0005	0.0002		d	474.490	19.933	−0.001	0.001	0.017
ip	374.979	0.1095	0.0008	0.0002		d	480.786	25.023	−0.001	0.001	0.017
ip	384.969	0.2204	0.0012	0.0002		w	480.785[b]	25.023	0.000	0.001	0.017
ip	394.974	0.4232	0.0017	0.0003		w	487.121	31.177	−0.002	0.002	0.019
ip	404.969	0.7762	0.0022	0.0003		w	493.493	38.565	−0.003	0.002	0.022
ip	414.966	1.3666	0.0026	0.0004		w	499.902	47.375	−0.003	0.002	0.021
ip	420.068	1.7972	0.0027	0.0005		w	506.351	57.817	0.000	0.003	0.021
d	422.148	2.0000	−0.0014	0.0001	0.124	w	512.842	70.120	0.002	0.003	0.021
ip	424.970	2.3174	0.0025	0.0006		w	519.377	84.533	0.002	0.004	0.015
d	427.764	2.6660	−0.0003	0.0002	0.076	w	525.954	101.325	0.002	0.005	0.013
ip	429.960	2.9764	0.0023	0.0007		w	532.573	120.79	0.01	0.01	0.014
d	436.087	3.9999	0.0003	0.0003	0.054	w	539.238	143.25	0.01	0.01	0.014
d	442.283	5.3330	0.0016	0.0003	0.053	w	545.943	169.02	0.00	0.01	0.011
d	451.482	7.9989	0.0022	0.0005	0.024	w	552.690	198.49	−0.01	0.01	0.012
d	458.373	10.666	0.000	0.001	0.022	w	559.485[b]	232.02	−0.07	0.01	0.013
d	463.935	13.332	−0.001	0.001	0.020						
						Methyl Glycolate[e]					
d	326.558	2.0030	0.0027	0.0002	0.033	d	365.566	13.314	0.002	0.001	0.033
d	339.616	4.0063	−0.0056	0.0003	0.025	d	371.015	16.677	−0.001	0.001	0.094
d	345.407	5.3346	−0.0131	0.0003	0.024	d	375.450	19.912	−0.005	0.001	0.100
d	353.911	7.9997	0.0169	0.0005	0.026	d	381.361	25.028	−0.006	0.001	0.107
d	360.342	10.648	0.009	0.001	0.027						

[a] ip refers to the inclined piston apparatus; 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; Δ*p* is the difference of the value of pressure, calculated with eq 8 and the parameters listed in Table 11, from the observed value of pressure; σ is the propagated error calculated from eq 3 or 4; Δ*T* is the difference between the boiling and condensation temperatures ($T_{boil} - T_{cond}$) for the sample. [b] Point excluded from Wagner-equation fit. [c] Vapor pressures from Ambrose et al. (1976). A = Ambrose et al. (1976). [d] The listed ebulliometric vapor pressures are those measured in the 1989 DIPPR Project 871 and reported by Steele et al. (1991b). [e] $\Delta p = p_{obs} - p_{Antoine}$ (Antoine equation fit) is the difference of the value of pressure, calculated value, from the observed value of pressure (see text).

The Wagner equation (Wagner, 1973) in the formulation given by Ambrose (1989)

$$\ln(p/p_c) = (1/T_r)[AY + BY^{1.5} + CY^{2.5} + DY^5] \quad (8)$$

where $T_r = T/T_c$, and $Y = (1 - T_r)$ was fitted to the measured vapor pressures (Table 1). As noted above, the critical pressure was included in the variables. The vapor-pressure fitting procedure including the minimization equation and the relative weightings is detailed by Steele (1995).

For fitting the two-phase heat capacities obtained in a cell of volume V_x, the experimental $C^{II}_{x,m}$ values (Table 8) were converted to $C^{II}_{V,m}$ by means of eq 7 for the cell expansion and the vapor-pressure fit for $(\partial p/\partial T)_{sat}$,

$$C^{II}_{V,m} = C^{II}_{V,m} - T/n\{(\partial V_x/\partial T)_x (\partial p/\partial T)_{sat}\} \quad (9)$$

The values of $C^{II}_{V,m}$ were used to derive functions for $(\partial^2 p/\partial T^2)_{sat}$ and $(\partial^2 \mu/\partial T^2)_{sat}$ [see eq 2 of Steele (1995)]. The functional form chosen for variation of the second derivative of the chemical potential with temperature was

$$(\partial^2 \mu/\partial T^2)_{sat}/J \cdot K^{-2} \cdot mol^{-1} = \sum_{i=0}^{n} (1 - T/T_c)^i \quad (10)$$

{For compounds where sufficient information was available to evaluate reliably $(\partial^2 \mu/\partial T^2)_{sat}$ [e.g., benzene (Goodwin, 1988) and toluene (Goodwin, 1989)], four terms (i.e., expansion to $n = 3$) were required to represent the function (Steele, 1995). Thus, four terms were used in this research.} Details of the weighting procedures, etc., are given in Steele (1995).

Estimates of liquid-phase molar volumes $V_m(l)$ for each compound were made with the extended corresponding-states equation (Riedel, 1954) as formulated by Hales and Townsend (1972):

$$(\rho/\rho_c) = 1.0 + 0.85 Y + (1.6916 + 0.9846\omega) Y^{1/3} \quad (11)$$

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. During each iteration a value of ω was obtained from the vapor-pressure fitting parameters and a corresponding value of ρ_c derived from the liquid-phase densities listed in Table 10.

Butyl Vinyl Ether and 1,2-Dimethoxyethane. For both butyl vinyl ether and 1,2-dimethoxyethane, critical temperatures and critical densities were determined from the dsc measurements. The critical temperatures were used in Wagner-equation fits to the vapor pressure measurements listed in Table 7. P_c was included in the variables in the fits. The procedure used resembled that of bicyclo[2.2.1]hept-2-ene except that no two-phase heat capacity measurements were included. For butyl vinyl ether, during each iteration a value of ω was obtained from the vapor-pressure fitting parameters and a corresponding value of ρ_c derived from the liquid-phase density at 298.15 K listed in Table 2. For 1,2-dimethoxyethane the liquid-phase densities (Sharipov et al., 1978) were used to derive ρ_c in each iteration.

5-Vinylbicyclo[2.2.1]hept-2-ene, trans-Azobenzene, Butyl acrylate, Di-tert-butyl ether, and Hexane-1,6-diol. For these five compounds, in the absence of measured values, both T_c and p_c were included in the variables in the fitting procedure. During each iteration a value of ω was obtained from the vapor-pressure fitting parameters and a corresponding value of ρ_c derived from the liquid-phase density at 298.15 K listed in Table 2.

Methyl Glycolate. For methyl glycolate the range of vapor pressure measurements (see Table 7) was so short that Wagner-equation fits were not attempted. For each

Table 8. Two-Phase (Solid + Vapor) or (Liquid + Vapor) Heat Capacities and Enthalpies of Fusion (R = 8.314 51 J·K^{-1}·mol^{-1})[a]

T/K	$C_{X,m}^{II}/R$	$C_{X,m}^{II}/R$	$C_{X,m}^{II}/R$	T/K	$C_{X,m}^{II}/R$	$C_{X,m}^{II}/R$	$C_{X,m}^{II}/R$
			Bicyclo[2.2.1]hept-2-ene[b]				
mass/g	0.010 854	0.015 016	0.023 820	mass/g	0.010 854	0.015 016	0.023 820
vol cell/cm^3	0.053 39	0.052 72	0.053 39	vol cell/cm^3	0.053 39	0.052 72	0.053 39
277.0	15.0	15.1	15.0	437.0	28.2	26.7	25.9
297.0	15.8	15.7	15.8	457.0	29.7	28.0	26.9
337.0	21.1	20.7	20.4	477.0	31.3	29.3	28.0
357.0	22.4	21.8	21.5	497.0	33.0	30.5	29.6
377.0	23.6	23.1	22.6	517.0	36.2	33.5	32.1
397.0	25.0	24.3	23.7	537.0	43.9	40.1	37.7
417.0	26.5	25.7	24.7	557.0	54.0	48.3	44.2

crystalline $C_{sat,m}/R = 0.0543T + 0.27$ (in temperature range 267 to 319.5 K)
liquid $C_{sat,m}/R = 0.0573T + 0.98$ (in temperature range 319.5 to 407 K)

$\Delta_c^l H_m(319.5 \text{ K}) = (3.5 \pm 0.2) \text{ kJ·mol}^{-1}$
$\Delta_c^l H_m^o(298.15 \text{ K}) = (3.2 \pm 0.2) \text{ kJ·mol}^{-1}$

T/K	$C_{X,m}^{II}/R$	T/K	$C_{X,m}^{II}/R$	T/K	$C_{X,m}^{II}/R$	T/K	$C_{X,m}^{II}/R$
			Butyl Vinyl Ether[c]				
315.0	25.6	375.0	29.7	435.0	32.9	495.0	37.0
335.0	28.0	395.0	30.9	455.0	34.1	515.0	39.6
355.0	28.9	415.0	31.9	475.0	35.2	535.0[d]	34.5
			1,2-Dimethoxyethane[e]				
315.0	23.7	375.0	24.8	435.0	28.4	495.0	31.9
335.0	24.0	395.0	26.2	455.0	28.9	515.0	34.1
355.0	24.7	415.0	27.3	475.0	30.1	535.0[d]	29.1
			Methyl Glycolate[f]				
315.0	23.9	355.0	24.7	335.0	24.3	375.0	25.1

T/K	$C_{X,m}^{II}/R$	$C_{X,m}^{II}/R$	T/K	$C_{X,m}^{II}/R$	$C_{X,m}^{II}/R$
		5-Vinylbicyclo[2.2.1]hept-2-ene			
mass/g	0.011 329	0.014 282	mass/g	0.011 329	0.014 282
vol cell/cm^3	0.052 72	0.053 39	vol cell/cm^3	0.052 72	0.053 39
315.0	25.4	25.5	375.0	29.2	29.3
335.0	26.5	26.8	395.0	30.6	30.5
355.0	27.7	28.1	415.0	32.2	32.0

T/K	$C_{X,m}^{II}/R$	T/K	$C_{X,m}^{II}/R$	T/K	$C_{X,m}^{II}/R$	T/K	$C_{X,m}^{II}/R$
			Butyl Acrylate[g]				
295.0	28.6	335.0	30.3	395.0	32.1		
315.0	29.5	375.0	32.1	415.0	33.8		
			trans-Azobenzene[h,i]				
275.0	25.2	395.0	39.3	495.0	46.3	595.0	51.4
295.0	27.2	415.0	41.1	515.0	47.2	615.0	52.6
315.0	29.2	435.0	42.5	535.0	48.3	635.0	54.2
355.0	37.2	455.0	43.6	555.0	49.5		
375.0	38.4	475.0	44.9	575.0	50.2		

crystalline $C_{sat,m}/R = 0.1011T - 2.264$ (in temperature range 265 to 341 K)
liquid $C_{sat,m}/R = 0.06687T + 13.18$ (in temperature range 341 to 425 K)

$\Delta_c^l H_m(341 \text{ K}) = (23.0 \pm 0.5) \text{ kJ·mol}^{-1}$
$\Delta_c^l H_m^o(298.15 \text{ K}) = (21.3 \pm 0.5) \text{ kJ·mol}^{-1}$

[a] Volume of cell is given at 298.15 K. [b] Measurements below 307 K were made with bicyclo[2.2.1]hept-2-ene in the solid phase. [c] Measurements made on a sample of mass 0.018 390 g in a cell of volume 0.053 39 cm^3. [d] Values not included in fit. Values are listed to show the large drop in heat capacity on passing into the fluid phase. [e] Measurements made on a sample of mass 0.020 819 g in a cell of volume 0.052 72 cm^3. [f] Measurements made on a sample of mass 0.031 311 g in a cell of volume 0.053 39 cm^3. [g] Measurements made on a sample of mass 0.017 627 g in a cell of volume 0.053 39 cm^3. [h] Measurements made on a sample of mass 0.021 531 g in a cell of volume 0.052 72 cm^3. [i] Measurements below 335 K were made with *trans*-azobenzene in the solid phase.

Table 9. 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
	Butyl Vinyl Ether		
185.5	534.8	283.9	539.9
220.1	538.8	340.8	536.0
	1,2-Dimethoxyethane		
200.7	532.9	291.3	536.7
260.6	536.6	385.9	533.6

compound the Antoine equation in the form

$$\log(p/p_{ref}) = A + B/\{(T/\text{K}) + C\} \qquad (12)$$

with p_{ref} = 1 kPa, was fit to the experimental vapor pressures.

Derived Results. General Comments. Table 11 lists the parameters derived using the various fitting procedures outlined above. Details of the fits to the vapor-pressure results are given in Table 7 (column 4 labeled Δp). Details of the fits of the measured liquid-phase densities for bicyclo-[2.2.1]hept-2-ene to extended corresponding states using the parameters listed in Table 11 are given in column 3 of Table 10.

For bicyclo[2.2.1]hept-2-ene values of $C_{V,m}^{II}(\rho = \rho_{sat})$ were derived from the parameters listed in Table 11 and
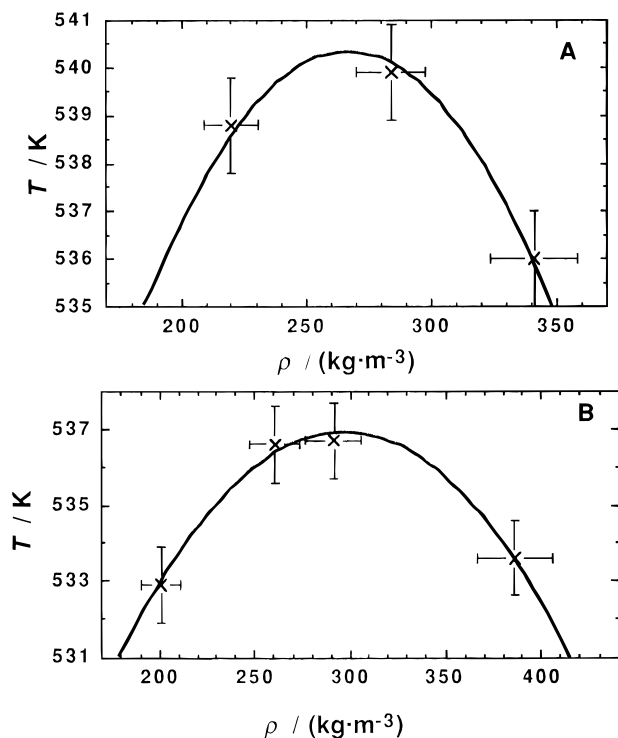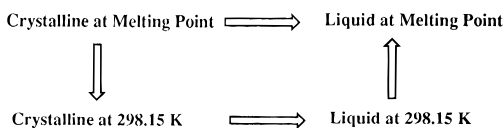
Figure 2. Vapor−liquid coexistence in the region of the critical point: (A) butyl vinyl ether; (B) 1,2-dimethoxyethane. The curves are drawn as an aid to the eye and do not represent any theoretically valid equation. The crosses span the range of uncertainty.

Figure 3. Thermochemical cycle relating $\Delta_l^g H_m$(melting point) to $\Delta_l^g H_m$(298.15 K).

Table 10. Measured Liquid-Phase Densities along the Saturation Line[a]

T/K	ρ/kg·m^{-3}	$100(\rho - \rho_{c.s.})/\rho$
	Bicyclo[2.2.1]hept-2-ene	
323.136	847.5	−0.06
348.131	822.4	−0.09
373.124	797.0	−0.03
398.118	770.6	0.08
423.113	741.5	0.03

[a] $\rho_{c.s.}$ is the density calculated using eq 11 and the parameters listed in Table 11.

corresponding $C_{sat,m}$ values derived using eq 6 of Steele et al. (1995). The results for $C_{sat,m}/R$ are reported in Table 12. The estimated uncertainty in these values is 1%.

Enthalpies of Vaporization. Enthalpies of vaporization $\Delta_l^g H_m$ were derived from the Wagner- and Antoine-equation fits (Table 11) using the Clapeyron equation:

$$dp/dT = \Delta_l^g H_m/(T\Delta_l^g V_m) \tag{13}$$

where $\Delta_l^g V_m$ is the increase in molar volume from the liquid to the real vapor.

Butyl Vinyl Ether, 1,2-Dimethoxyethane, Bicyclo[2.2.1]hept-2-ene, 5-Vinylbicyclo[2.2.1]hept-2-ene, trans-Azobenzene, Butyl Acrylate, Di-tert-butyl Ether, and Hexane-1,6-diol. For each of these compounds estimates

Table 11. Parameters for Equations 8 and 10, Critical Constants, and Acentric Factors

	Butyl Vinyl Ether				1,2-Dimethoxyethane		
A	−8.047 44			A	−8.089 80		
B	2.311 58			B	2.535 55		
C	−2.914 99			C	−3.480 91		
D	−4.095 65			D	−3.650 36		
T_c	540.5 K	p_c	3200 kPa	T_c	537 K	p_c	3960 kPa
ρ_c	261.1 kg·m^{-3}	ω	0.3575	ρ_c	293.2 kg·m^{-3}	ω	0.3592
	Bicyclo[2.2.1]hept-2-ene				5-Vinylbicyclo[2.2.1]hept-2-ene		
A	−7.589 82	b_0	−0.396 61	A	−7.703 72		
B	3.252 77	b_1	−0.355 75	B	2.247 69		
C	−3.617 18	b_2	0.291 78	C	−2.859 91		
D	−1.334 69			D	−3.199 60		
T_c	590 K	p_c	4860 kPa	T_c	620 K	p_c	3300 kPa
ρ_c	299.5 kg·m^{-3}	ω	0.1937	ρ_c	291.3 kg·m^{-3}	ω	0.2970
	trans-Azobenzene				Butyl Acrylate		
A	−10.485 19			A	−7.590 83		
B	6.498 10			B	1.969 32		
C	−6.862 49			C	−3.058 37		
D	−1.889 64			D	−4.176 04		
T_c	830 K	p_c	3770 kPa	T_c	644 K	p_c	4540 kPa
ρ_c	300 kg·m^{-3}	ω	0.5018	ρ_c	299.8 kg·m^{-3}	ω	0.3119
	Di-*tert*-butyl Ether				Hexane-1,6-diol		
A	−7.257 46			A	−13.840 35		
B	1.908 94			B	11.997 82		
C	−4.032 15			C	−19.153 71		
D	−1.574 01			D	−1.563 93		
T_c	555 K	p_c	2425 kPa	T_c	700 K	p_c	3000 kPa
ρ_c	259.8 kg·m^{-3}	ω	0.2819	ρ_c	294 kg·m^{-3}	ω	0.9411

Antoine Equation Coefficients Methyl Glycolate	
P_{ref}/kPa	1
A	6.497 99
B	−1578.06
C	−71.9043
range/K[b]	326−405

[a] The parameters listed in this table are those derived from the fitting procedures. [b] Temperature range of the vapor pressures used in the fit.

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	$C_{sat,m}/R$
	Bicyclo[2.2.1]hept-2-ene		
340.0	20.4	480.0	28.1
360.0	21.6	500.0	29.3
380.0	22.7	520.0	30.8
400.0	23.8	540.0	32.7
420.0	24.9	560.0	36.0
440.0	25.9	580.0	47.0
460.0	27.0		

of the liquid-phase volumes were made using eq 11 and the parameters given in Table 11. 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 (Pitzer and Curl, 1957), and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera (1983). This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene and toluene (Chirico and Steele, 1994). Third virial coefficients are required for accurate calculation of the gas volume for pressures greater than 1 bar. Uncertainties in the virial coefficients were assumed to be 10%.

Methyl Glycolate. The absence of critical properties precluded using the methodology outlined for the other compounds listed in the previous section. For methyl glycolate, liquid-phase volumes were derived using the density at 298.15 K and the coefficient of expansion listed in Table 2. Second virial coefficients were estimated with the correlation by Scott et al. (1950). Since enthalpies of

vaporization were not derived for pressures greater than 1 bar, third virials were neglected. Uncertainties in both the liquid-phase molar volumes and virial coefficients were assumed to be 20%.

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.

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. In Table 14 the enthalpies of vaporization, $\Delta_l^g H_m$, have been converted to the corresponding values for the ideal gas, $\Delta_l^g H_m$, using the following estimates of $(H^o - H)$ in kJ·mol^{-1} for the real gas at its saturation vapor pressure at 298.15 K: butyl vinyl ether, 0.07; 1,2-dimethoxyethane, 0.07; bicyclo[2.2.1]hept-2-ene, 0.05; 5-vinylbicyclo[2.2.1]hept-2-ene, 0.02; and di-*tert*-butyl ether, 0.07; the corrections for the less volatile compounds were assumed to be negligibly small. These corrections were calculated using eq 20 of Chirico et al. (1993) and the virial coefficients derived above.

In the next section of the paper the results obtained for each compound are discussed and compared with available literature values and relevant group-contribution parameters are derived.

Discussion

Butyl Vinyl Ether. A value for the enthalpy of combustion of butyl vinyl ether, $\Delta_c H_m^o/M = -(3857.2 \pm 0.8)$ kJ·mol^{-1} has been reported in the literature (Trofimov et al., 1981). Trofimov et al., gave no details of the combustion calorimetry or the purity of the sample. The result is somewhat lower than the value, $\Delta_c H_m^o = -(3860.20 \pm 1.12)$ kJ·mol^{-1} obtained in this research, and the difference may be due to the presence of water in their sample. The presence of 0.08 mol % water in the sample used (Trofimov et al., 1981) would reconcile both sets of results.

Trofimov et al. reported an enthalpy of vaporization at 298.15 K of (34.3 ± 2.5) kJ·mol^{-1}. That value agrees, within their stated uncertainty limits, with the value obtained here $\Delta_l^g H_m = (36.66 \pm 0.23)$ kJ·mol^{-1}.

A search of the literature through June 1996 failed to find any experimentally determined values for the critical properties of butyl vinyl ether to compare with those obtained in the present research using the dsc.

Addition of the group-additivity parameters from Benson (1976) and Reid et al. (1987) plus the C−(C)$_2$(H)$_2$ group parameter derived for alcohols by Steele et al. (1991b) to estimate the enthalpy of formation of butyl vinyl ether follows:

1	C$_d$−(C$_d$)(H)$_2$	26.21 × 1	26.21
1	C$_d$−(C$_d$)(O)(H)	43.12 × 1	43.12
1	C−(O)(C)(H)$_2$	−33.91 × 1	−33.91
2	C−(C)$_2$(H)$_2$	−20.21 × 2	−40.42
1	C−(C)(H)$_3$	−42.25 × 1	−42.25
1	O−(C)(C$_d$)	−133.56 × 1	−133.56
	$\Delta_f H_m^o$(C$_6$H$_{12}$O, g, 298.15 K)		−180.8 kJ·mol^{-1}

The value determined in this research is $\Delta_f H_m^o$(C$_6$H$_{12}$O, g, 298.15 K) $-(179.2 \pm 1.2)$ kJ·mol^{-1} (Table 14). The agreement is excellent, showing that no group-additivity parameters need revision.

1,2-Dimethoxyethane. A search of the literature through June 1996 failed to find a previous determination of the ideal gas standard enthalpy of formation of 1,2-dimethoxyethane. The search did produce references to determinations of its vapor pressure (Stull, 1947; Kobe et al., 1956; Sharippov and Bairamova, 1978), critical properties (Kobe et al., 1956; Quadri and Kudchaker, 1991), heat

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

T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}
	Butyl Vinyl Ether		
260.0[b]	39.16 ± 0.27	360.0	32.53 ± 0.32
280.0[b]	37.79 ± 0.25	380.0	31.12 ± 0.42
298.15[b]	36.59 ± 0.23	400.0	29.60 ± 0.57
300.0[b]	36.47 ± 0.23	420.0[b]	27.94 ± 0.73
320.0	35.18 ± 0.23	440.0[b]	26.10 ± 0.93
340.0	33.88 ± 0.25	460.0[b]	24.04 ± 1.16
	1,2-Dimethoxyethane		
260.0[b]	39.29 ± 0.27	360.0	32.46 ± 0.33
280.0[b]	37.91 ± 0.25	380.0	30.95 ± 0.43
298.15[b]	36.69 ± 0.23	400.0[b]	29.33 ± 0.58
300.0[b]	36.58 ± 0.23	420.0[b]	27.57 ± 0.75
320.0	35.24 ± 0.23	440.0[b]	25.64 ± 0.96
340.0	33.87 ± 0.27	460.0[b]	23.50 ± 1.20
	Bicyclo[2.2.1]hept-2-ene		
280.0[b,c]	35.83 ± 0.22	380.0	30.82 ± 0.30
298.15[b,c]	35.00 ± 0.20	400.0	29.62 ± 0.40
300.0[b,c]	34.92 ± 0.20	420.0[b]	28.34 ± 0.52
320.0[b]	33.98 ± 0.18	440.0[b]	26.96 ± 0.65
340.0	32.99 ± 0.20	460.0[b]	25.50 ± 0.80
360.0	31.94 ± 0.25		
	5-Vinylbicyclo[2.2.1]hept-2-ene		
260.0[b]	44.67 ± 0.32	380.0	37.42 ± 0.27
280.0[b]	43.39 ± 0.30	400.0	36.18 ± 0.32
298.15[b]	42.27 ± 0.27	420.0	34.89 ± 0.40
300.0[b]	42.15 ± 0.27	440.0[b]	33.51 ± 0.52
320.0	40.97 ± 0.25	460.0[b]	32.02 ± 0.67
340.0	39.79 ± 0.23	480.0[b]	30.42 ± 0.83
360.0	38.62 ± 0.23		
	Methyl Glycolate		
290.0[b]	53.4 ± 7.0	340.0	48.5 ± 4.5
298.15[b]	52.5 ± 6.3	360.0	47.0 ± 4.2
300.0[b]	52.3 ± 6.2	380.0	45.6 ± 4.0
320.0[b]	50.2 ± 5.1	400.0[b]	44.2 ± 4.0
	trans-Azobenzene		
298.15[b,c]	72.75 ± 0.68	540.0	55.68 ± 0.43
400.0[b]	65.43 ± 0.48	560.0	54.21 ± 0.48
420.0[b]	64.04 ± 0.45	580.0	52.71 ± 0.58
440.0	62.66 ± 0.43	600.0	51.16 ± 0.68
460.0	61.28 ± 0.42	620.0	49.56 ± 0.83
480.0	59.91 ± 0.40	640.0[b]	47.90 ± 1.00
500.0	58.52 ± 0.38	660.0[b]	46.17 ± 1.18
520.0	57.11 ± 0.40	680.0[b]	44.36 ± 1.40
	Butyl Acrylate		
260.0[b]	50.35 ± 0.42	380.0	41.42 ± 0.27
280.0[b]	48.72 ± 0.37	400.0	40.00 ± 0.30
298.15[b]	47.31 ± 0.33	420.0	38.54 ± 0.35
300.0[b]	47.17 ± 0.33	440.0[b]	37.01 ± 0.45
320.0	45.68 ± 0.30	460.0[b]	35.39 ± 0.57
340.0	44.23 ± 0.28	480.0[b]	33.66 ± 0.72
360.0	42.83 ± 0.27		
	Di-*tert*-butyl Ether		
280.0[b]	38.33 ± 0.27	340.0	34.63 ± 0.25
298.15	37.27 ± 0.23	360.0	33.21 ± 0.30
300.0	37.17 ± 0.23	380.0	31.65 ± 0.40
320.0	35.94 ± 0.23	400.0[b]	29.95 ± 0.57
	Hexane-1,6-diol		
298.15[b,c]	98.5 ± 1.8	460.0	70.4 ± 0.6
300.0[b,c]	98.2 ± 1.8	480.0	67.0 ± 0.6
320.0[b]	94.7 ± 1.5	500.0	63.5 ± 0.6
340.0[b]	91.3 ± 1.3	520.0	60.0 ± 0.7
360.0	87.8 ± 1.1	540.0	56.5 ± 0.8
380.0	84.3 ± 1.0	560.0	53.1 ± 1.0
400.0	80.8 ± 0.9	580.0[b]	49.7 ± 1.3
420.0	77.3 ± 0.8	600.0[b]	46.4 ± 1.6
440.0	73.9 ± 0.7		

[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 or Antoine equations. [c] The value at this temperature is for the supercooled liquid.

capacity (Kusano et al., 1973), density (Carvajal et al., 1965; Sharippov and Bairamova, 1978; Kusano, 1978;

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

	$\Delta_f H_m^\circ(c)$/kJ·mol^{-1}	$\Delta_c^l H_m^\circ$/kJ·mol^{-1}	$\Delta_f H_m^\circ(l)$/kJ·mol^{-1}	$\Delta_l^g H_m^\circ$/kJ·mol^{-1}	$\Delta_f H_m^\circ(g)$/kJ·mol^{-1}
A			-215.84 ± 1.18	36.66 ± 0.23	-179.2 ± 1.2
B			-379.56 ± 0.64	36.76 ± 0.23	-342.8 ± 0.7
C			-609.41 ± 0.94	52.5 ± 6.3	-556.9 ± 6.4
D	44.44 ± 2.00	3.2 ± 0.2	47.6 ± 2.1	35.05 ± 0.20	$82.6_5 \pm 2.1$
E			116.50 ± 0.88	42.29 ± 0.27	158.8 ± 0.9
F	311.41 ± 1.04	21.3 ± 0.5	332.7 ± 1.2	72.75 ± 0.68	405.5 ± 1.3
G			-422.59 ± 0.70	47.31 ± 0.33	-375.3 ± 0.8
H			-398.45 ± 0.72	37.34 ± 0.23	-361.1 ± 0.8
I	-583.86 ± 0.72	21.6 ± 1.0	-562.3 ± 1.2	98.5 ± 1.8	-463.8 ± 2.2

^{a} A = Butyl vinyl ether, B = 1,2-dimethoxyethane, C = methyl glycolate, D = bicyclo-[2.2.1]hept-2-ene, E = 5-vinyl-bicyclo[2.2.1]hept-2-ene, F = *trans*-azobenzene, G = butyl acrylate, H = di-*tert*-butyl ether and I = hexane-1,6-diol. ^{b} Hexane-1,6-diol enthalpy of formation for the crystalline solid and enthalpy of fusion determined in 1989 DIPPR Project 871 and reported by Steele et al. (1991b).
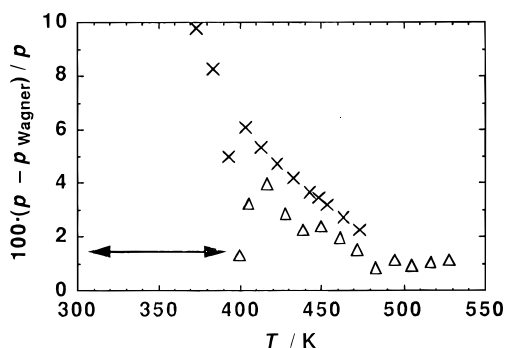
Figure 4. Comparison of literature vapor pressures for 1,2-dimethoxyethane with those obtained using the Wagner equation and the parameters listed in Table 11: ($\triangle$) Kobe et al. (1956); ($\times$) Sharipov and Bairamova (1978). The double-headed arrow represents the range of the measurements of this research and of those reported in Table 7.
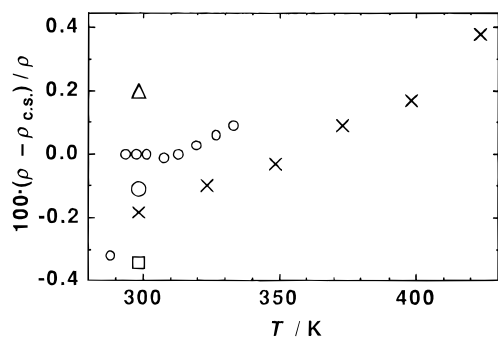
Figure 5. Comparison of literature density measurements for 1,2-dimethoxyethane with values obtained by extended corresponding states using eq 11: ($\triangle$) Kusano (1978); ($\bigcirc$) Table 3 (Sharipov and Bairamova, 1978); ($\times$) PvT measurements of Sharipov and Bairamova (not included is the point at 473 K where the deviation was 1.41%); ($\bigcirc$) Werblan and Leinski (1980); ($\square$) Carvajal et al. (1965).

Werblan and Leinski, 1980), and enthalpy of vaporization (Kusano and Wadsö, 1970).

Figure 4 compares two sets of vapor pressure measurements reported in the literature (Kobe et al., 1956; Sharippov and Bairamova, 1978) with values obtained using the Wagner equation and the parameters listed in Table 11. The values (Stull, 1947) were not included in the plot because they deviated by so much from those obtained in this research (the deviations ranged from +61% at 225 K to -28.3% at 366 K and were approximately linear within that temperature interval).

Kobe et al. (1956) and Quadri and Kudchadker (1991) both measured critical properties for 1,2-dimethoxyethane. Results are compared in Table 15. Agreement in T_c and p_c values is good (± 2 K), but the critical density obtained (Kobe et al., 1956) is 14% high.

Kusano et al. (1973) list a heat capacity C_p/R = 23.25 at 298.15 K in excellent agreement with that obtained in this

Table 15. Comparison of Literature Values of the Critical Properties of 1,2-Dimethoxyethane with Values Obtained in This Research

reference	T_c/K	p_c/kPa	ρ_c/kg·m^{-3}
Kobe et al., 1956	536	3871	333
Quadri and Kudchadker, 1991	539.2 ± 0.4	3860 ± 20	
this research	537 ± 1	3960 ± 100	293 ± 10

research, C_{sat}/R = 23.3 at 298.15 K (Tables 2 and 8).

Figure 5 compares values for the density of 1,2-dimethoxyethane found in a search of the literature (Carvajal et al., 1965; Kusano, 1978; Sharipov and Bairamova, 1978; Werblan and Leinski, 1980) with values calculated using extended corresponding states (eq 11) and the parameters listed in Table 11. The density measured during the combustion calorimetric measurements 862.0 kg·m^{-3} at 298.15 K was used to determine ρ_c and consequently matches exactly that derived using eq 11.

Kusano and Wadsö (1970) measured the enthalpy of vaporization of 1,2-dimethoxyethane at 298.15 K using a vaporization calorimeter. Their result $\Delta_l^g H_m^\circ$(298.15 K) = (36.39 ± 0.20) kJ·mol^{-1} is in agreement with the value obtained in this research of (36.69 ± 0.23) kJ·mol^{-1} (Table 14). Kusano and Wadsö derived an enthalpy of vaporization of 31.2 kJ·mol^{-1} from the vapor pressure measurements listed by Stull (1947). That result provides corroborating evidence that the vapor pressures listed by Stull are in error.

Addition of the group-additivity parameters (Benson, 1976; Reid et al., 1987) to estimate the enthalpy of formation of 1,2-dimethoxyethane follows:

2	C$-$(O)(H)$_3$	-42.39×2	-84.78
2	C$-$(O)(C)(H)$_2$	-33.91×2	-67.82
2	O$-$(C)$_2$	-99.23×2	-198.46
	$\Delta_f H_m^\circ$(C$_4$H$_{10}$O$_2$, g, 298.15 K)		-351.06 kJ·mol^{-1}

The value determined in this research is $\Delta_f H_m^\circ$(C$_4$H$_{10}$O$_2$, g, 298.15 K) $-(342.8 \pm 0.7)$ kJ·mol^{-1} (Table 14). The difference, 8.3 kJ·mol^{-1}, is larger than normal (<4 kJ·mol^{-1}) and may signify that one or more of the group-additivity parameters need revision. In unpublished work at NIPER the O$-$(C)$_2$ group was assigned a value of -97.07 kJ·mol^{-1} and the C$-$(O)(H)$_3$ group assigned the same value as the group C$-$(C)(H)$_3$, namely, -42.25 kJ·mol^{-1}. Those changes would decrease the difference to 3.7 kJ·mol^{-1}. In addition there probably should be a 1,4-(O,O)-interaction parameter included in the summation of the groups. Unpublished work at NIPER appears to assign a value of $+4$ kJ·mol^{-1} to the 1,4-(O,O)-interaction parameter. However, further enthalpy of formation measurements on straight chain alkyl ethers will be required to resolve the discrepancies and "firm-up" the above assigned group values. The work of Fenwick et al. (1975) represents the "best" measurements published to date. In that work only four of the eight ethers studied had straight chain alkyl groups.

Table 16. Comparison of Literature Values for the Enthalpies of Combustion, Formation, and Sublimation with Values Obtained in This Research

reference	$-\Delta_c H^o_m/\text{kJ·mol}^{-1}$	$\Delta_f H^o_m(c)/\text{kJ·mol}^{-1}$	$\Delta^g_c H^o_m/\text{kJ·mol}^{-1}$	$\Delta_f H^o_m(g)/\text{kJ·mol}^{-1}$
		Bicyclo[2.2.1]hept-2-ene		
Kozina et al., 1976	4225.13 ± 1.34	41.41 ± 1.34	38.70 ± 0.54	80.1 ± 1.4
Hall et al., 1973	4213.5 ± 1.7	29.8 ± 1.7	33.60 ± 0.08	63.4 ± 1.8
Steele, 1978	4237.2 ± 3.2	53.5 ± 3.2	37.7 ± 0.9	91.2 ± 3.3
Walsh and Wells, 1976				88.4 ± 2.7
this research	4228.16 ± 1.96	44.44 ± 2.00	38.25 ± 0.28	$82.6_5 \pm 2.1$
		trans-Azobenzene		
Cole and Gilbert, 1951	6471.8 ± 1.7	320.5 ± 1.7		
Schulze et al., 1977	6462.6 ± 3.0	311.3 ± 1.7	93.84 ± 0.12	405.1 ± 1.7
Dias et al., 1992	6459.9 ± 1.0	308.6 ± 1.9	93.84 ± 0.12	402.5 ± 1.9
this research	6462.7 ± 0.9	311.4 ± 1.0	94.05 ± 0.84	405.5 ± 1.3
		Di-*tert*-butyl Ether		
Smutny and Bondi, 1961	5308.2 ± 1.0			-364.8 ± 1.3
Fenwick et al., 1975	5320.95 ± 1.08			-362.0 ± 1.6
this research	5322.1 ± 0.61			-361.1 ± 0.8

Methyl Glycolate. A search of the literature through June 1993 failed to find any thermochemical or thermophysical property measurements on methyl glycolate.

Addition of the group-additivity parameters (Benson, 1976, and Reid et al., 1987) plus the O-(CO)(C) group parameter derived in (Steele et al., 1991b and Steele et al., 1994b) to estimate the enthalpy of formation of methyl glycolate follows:

1	C−(O)(H)$_3$	-42.39×1	-42.39
1	O−(CO)(C)	-179.70×1	-179.70
1	CO−(O)(C)	-146.96×1	-146.96
1	O−(C)(H)	-158.68×1	-158.68
1	C−(O)(CO)(H)$_2$		
	$\Delta_f H^o_m(\text{C}_3\text{H}_6\text{O}_3, \text{g}, 298.15 \text{ K})$		$-527.73 \text{ kJ·mol}^{-1}$

The value determined in this research is $\Delta_f H^o_m(\text{C}_3\text{H}_6\text{O}_3, \text{g}, 298.15 \text{ K}) -(556.9 \pm 6.4) \text{ kJ·mol}^{-1}$ (Table 14). Hence the C−(O)(CO)(H)$_2$ group parameter is derived as -29.2 kJ·mol^{-1}.

Bicyclo[2.2.1]hept-2-ene. Thermochemical studies on bicyclo[2.2.1]hept-2-ene have been reported by several groups (Hall et al., 1973; Kozina et al., 1978; Steele, 1978). In addition Walsh and Wells (1976) measured equilibrium constants for the reaction

$$\text{C}_5\text{H}_6(\text{g}) + \text{C}_2\text{H}_4(\text{g}) \rightleftharpoons \text{C}_7\text{H}_{10}(\text{g}) \qquad (14)$$
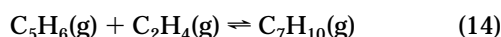
Using values for the thermodynamic properties of cyclopentadiene and ethylene and statistical thermodynamic calculation of $(G^\circ(T) - H^\circ(298.15 \text{ K}))/T$ for bicyclo[2.2.1]-hept-2-ene, they obtained a standard ideal-gas enthalpy of formation for that compound. The results of the thermochemical studies and equilibrium measurements are summarized in Table 16. The results show the need for a definitive answer for the condensed-phase and ideal-gas enthalpies of formation for bicyclo[2.2.1]hept-2-ene.

Combustion calorimetric measurements on bicyclo[2.2.1]-hept-2-ene have been plagued by its relatively high vapor pressure at 298.15 K resulting in vaporization of sample either prior to or during combustion. In the study reported here it would appear that not all the sample was burned during each combustion since the CO_2 recovery was only 99.7% on average (see Table 2). Hence, in this case the results of the measurements were determined on the basis of the actual CO_2 recovery for each experiment. The results $\Delta_c H^o_m = (4228.16 \pm 1.96) \text{ kJ·mol}^{-1}$ and $\Delta_f H^o_m(c) = (44.44 \pm 2.00) \text{ kJ·mol}^{-1}$ differ from each of the other combustion calorimetric studies and would appear to add yet another value to the pool of results for this compound. However, see below in the discussion of the results for 5-vinylbicyclo-[2.2.1]hept-2-ene where sample containment problems were not present.
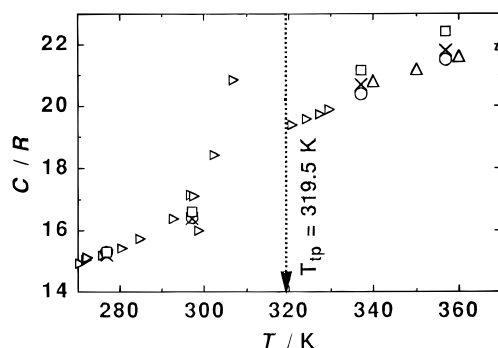

Figure 6. Comparison of bicyclo[2.2.1]hept-2-ene dsc heat capacity measurements and derived values (Tables 8 and 12) with the values of Lebedev et al. (1992): ($\triangle$) C_{sat}/R values (see Table 12); ($\square$) 0.010 854 g $C^{II}_{X,m}/R$ values (Table 8); ($\times$) 0.015 016 g $C^{II}_{X,m}/R$ values (Table 8); ($\bigcirc$) 0.023 820 g $C^{II}_{X,m}/R$ values (Table 8); (sideways triangle) C_{sat}/R values of Lebedev et al.
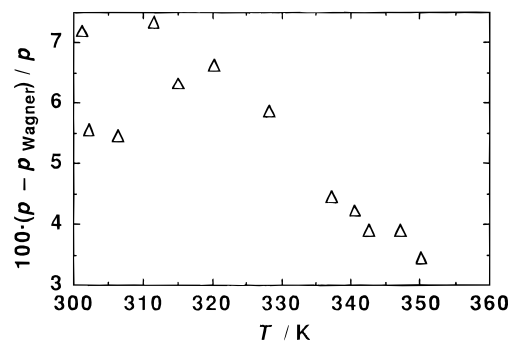

Figure 7. Comparison of literature vapor pressures for bicyclo[2.2.1]hept-2-ene with those obtained using the Wagner equation and the parameters listed in Table 11: ($\triangle$) Hall et al. (1973). The temperature range of the measurements of this research reported in Table 7 is 338.66 K to 406.75 K.

As part of a study of the thermodynamics of polymerization of bicyclo[2.2.1]hept-2-ene, Lebedev et al. (1992) measured its heat capacity in the range 10 to 330 K, the triple point temperature, and the enthalpy of fusion. Figure 6 compares the heat capacity measurements obtained by Lebedev et al. (1992) with those determined at NIPER using the dsc and reported in Table 8. The agreement is good, as is a comparison of the measured triple points and enthalpies of fusion: $T_{\text{t.pt.}} = (319.45 \pm 0.05)$ K (Lebedev et al.), (319.5 ± 0.2) K (NIPER); $\Delta^l_c H^o_m(T_{\text{t.pt.}}) = (3.48 \pm 0.06) \text{ kJ·mol}^{-1}$ (Lebedev et al.), $(3.5 \pm 0.2) \text{ kJ·mol}^{-1}$ (NIPER) (Table 8).

Figure 7 compares liquid-phase vapor pressures for bicyclo[2.2.1]hept-2-ene obtained by Hall et al. (1973) with those derived using the Wagner equation and the param-
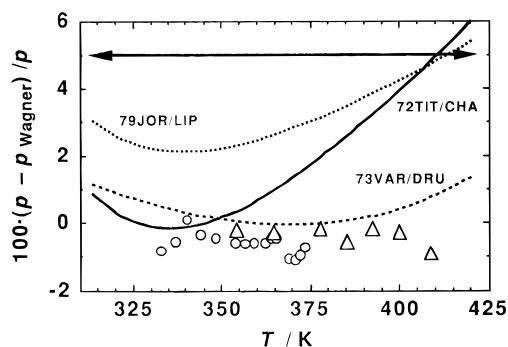
Figure 8. Comparison of literature vapor pressures for 5-vinylbicyclo[2.2.1]hept-2-ene with those obtained using the Wagner equation and the parameters listed in Table 11: (△) Varushchenko et al. (1974); (○) Figurski and von Weber (1976). The double-headed arrow represents the range of the measurements of this research and of those reported in Table 7. The curves represent the Antoine equations reported by Titova et al. (1972), Varushchenko et al. (1974), and Jordache et al. (1979).

eters listed in Table 11. Hall et al. noted (implying *no* enthalpy change on fusion) that there were "no discontinuities in the vapor pressure plots for the solid hydrocarbons at their melting points".

The enthalpy of sublimation obtained in this research $\Delta_c^g H_m^o(C_7H_{10}, 298.15\ K) = (38.25 \pm 0.28)$ kJ·mol^{-1} agrees with both the (38.70 ± 0.54) kJ·mol^{-1} obtained by Kozina et al. (1976) in a Calvet microcalorimeter and the (37.7 ± 0.9) kJ·mol^{-1} obtained by Steele from vapor pressure measurements (Steele, 1978). Jochems et al. (1982) using an LKB vaporization calorimeter obtained a value $\Delta_c^g H_m^o(C_7H_{10}, 298.15\ K) = (37.84 \pm 0.14)$ kJ·mol^{-1}.

Accepting only the measurements made in the NIPER research, a ring strain energy (or ring-correction parameter) for bicyclo[2.2.1]hept-2-ene based on the group-additivity parameters listed (Benson, 1976; Reid et al., 1987) is calculated as follows:

2	C—(C$_d$)(C)$_2$(H)	-6.20×2	-12.40
2	C$_d$—(C$_d$)(C)(H)	35.96×2	71.92
3	C—(C)$_2$(H)$_2$	-20.72×3	-62.16
1	ring strain		
	$\Delta_f H_m^o(C_7H_{10},$ g, 298.15 K)		-2.64 kJ·mol^{-1}

The value determined in this research is: $\Delta_f H_m^o(C_7H_{10},$ g, 298.15 K) = $(82.6_5 \pm 2.1)$ kJ·mol^{-1} (Table 14). Hence the ring strain or ring-correction parameter is derived as 85.3 kJ·mol^{-1}.

5-Vinylbicyclo[2.2.1]hept-2-ene. 5-Vinylbicyclo[2.2.1]-hept-2-ene exists as *exo* and *endo* isomers. Although it was not precisely determined if the sample used in the calorimetric measurements was either a pure isomer or a mixture of both, the small difference between the boiling and condensation temperatures in the ebulliometric vapor pressure measurements (0.010 K, Table 7) points to the compound being a single isomer or to both isomers having very similar vapor pressures. It was noted that both Varushchenko et al. (1973) and Inque (1987) analyzed their samples of 5-vinylbicyclo[2.2.1]hept-2-ene as containing both *exo* and *endo* isomers in the approximate ratio of 1:2 and 2:3, respectively.

Several studies on the vapor pressure of 5-vinylbicyclo[2.2.1]hept-2-ene have been reported in the literature (Titiva et al., 1972; Varushchenko et al., 1973; Varushchenko et al., 1974; Figurski and von Weber, 1976; Jordache et al. 1979). Figure 8 compares the results of the various studies with values obtained using the Wagner vapor pressure equation and the parameters listed in Table 11. The results of the study (Varushchenko et al., 1973) were obtained from a copy of the VINITI deposited docu-

Table 17. Comparison of Literature Values of the Density with Values from Corresponding States

		ρ/kg·m^{-3}	
reference	T/K	lit.	corr states
5-Vinylbicyclo[2.2.1]hept-2-ene			
Figurski and von Weber, 1976	323	862	862.1
Figurski and von Weber, 1976	348	840	839.1
Figurski and von Weber, 1976	358	830	829.6
Jordache et al., 1979	293	886	888.8
Butyl Acrylate			
Papayoanou and Christopulos, 1973	273.15	914.0	913.9
Papayoanou and Christopulos, 1973	283.15	905.7	905.7
Papayoanou and Christopulos, 1973	293.15	897.3	897.4
Papayoanou and Christopulos, 1973	303.15	888.9	889.0
Papayoanou and Christopulos, 1973	313.15	880.5	880.6
Papayoanou and Christopulos, 1973	323.15	872.0	872.0
Papayoanou and Christopulos, 1973	333.15	863.4	863.4
Di-tert-butyl Ether			
Smutny and Bondi, 1961	293	762.2	762.4
Fenwick et al., 1975	298.15	761	757.7
Obama et al., 1985	288.15	766.9	766.8
Obama et al., 1985	298.15	757.8	757.7
Obama et al., 1985	308.15	748.7	748.5
Table 2	298.15	757.8	757.7

ment. Only the boiling point and enthalpy of vaporization were reported by Varushchenko et al. (1974). Varushchenko et al. (1973, 1974) state that their results were for a 35% *exo*, 65% *endo* mixture of 5-vinylbicyclo[2.2.1]hept-2-ene.

Figurski and von Weber (1976) also determined densities at various temperatures for 5-vinylbicyclo[2.2.1]hept-2-ene which are compared in Table 17 with values calculated using extended corresponding states (eq 11) and the parameters listed in Table 11. Agreement is excellent. Jordache et al. (1979) reported a density of 886.0 kg·m^{-3} at 293 K compared to a calculated value of 888.8 kg·m^{-3} obtained using extended corresponding states (eq 11) and the parameters listed in Table 11.

The ideal-gas enthalpy of vaporization $\Delta_l^g H_m^o(C_9H_{12},$ 298.15 K) = (42.68 ± 1.17) kJ·mol^{-1} obtained by Varushchenko et al. (1973, 1974) is in good agreement with the value (42.29 ± 0.27) kJ·mol^{-1} obtained in this research (see Table 13 and text). Titova et al. list (Titova et al., 1972) $\Delta_l^g H_m^o(C_9H_{12},$ 298.15 K) = 43.14 kJ·mol^{-1} and $\Delta_l^g H_m^o(C_9H_{12},$ 323 K) = 41.5 kJ·mol^{-1}. In this research (Table 13) a value $\Delta_l^g H_m^o(C_9H_{12},$ 323 K) = (40.8 ± 0.3) kJ·mol^{-1} was obtained.

A ring strain energy (or ring-correction parameter) for 5-vinylbicyclo[2.2.1]hept-2-ene based on the group-additivity (Benson, 1976; Reid et al., 1987) is calculated as follows:

1	C$_d$—(C$_d$)(H)$_2$	26.21×1	26.21
3	C$_d$—(C$_d$)(C)(H)	35.96×3	107.88
3	C—(C$_d$)(C)$_2$(H)	-6.2×3	-18.60
2	C—(C)$_2$(H)$_2$	-20.72×2	-41.44
1	ring strain		
	$\Delta_f H_m^o(C_9H_{12},$ g, 298.15 K)		74.05 kJ·mol^{-1}

The value determined in this research is $\Delta_f H_m^o(C_9H_{12},$ g, 298.15 K) = (158.8 ± 0.9) kJ·mol^{-1} (Table 14). Hence the ring strain or ring-correction parameter is derived as 84.75 kJ·mol^{-1}.

The excellent agreement between the ring correction parameter derived for bicyclo[2.2.1]hept-2-ene, 85.3 kJ·mol^{-1}, and the value derived for 5-vinylbicyclo[2.2.1]hept-2-ene, 84.75 kJ·mol^{-1}, adds weight to the derived enthalpies of formation of bicyclo[2.2.1]hept-2-ene obtained in this research. A ring-correction parameter of 84.9 kJ·mol^{-1} was derived as a weighted mean of both values.
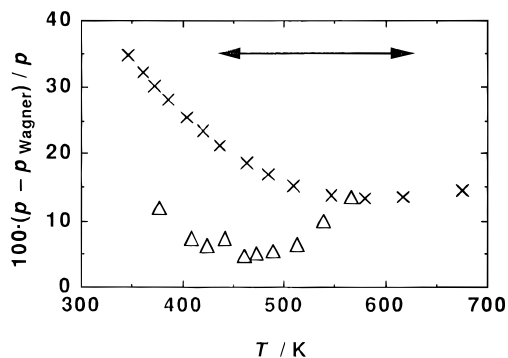
Figure 9. Comparison of literature vapor pressures for *trans*-azobenzene with those obtained using the Wagner equation and the parameters listed in Table 11: (△) Stull (1947); (×) Engineering Sciences Data Item (1978). The double-headed arrow represents the range of the measurements of this research and of those reported in Table 7.
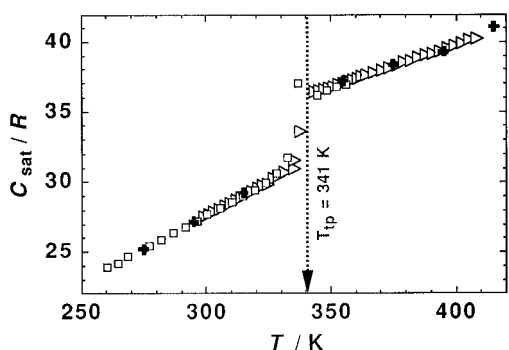

Figure 10. Comparison of *trans*-azobenzene dsc heat capacity measurements with literature values: (+) dsc $C_{X,m}^{II}/R$ values (Table 8); (□) van Miltenburgh and Bouwstra (1984); (sideways triangle) Bouwstra et al. (1985).

trans-Azobenzene. Thermochemical studies on *trans*-azobenzene have been reported by several groups (Coruccini and Gilbert, 1939; Cole and Gilbert, 1951; Schulze et al., 1977; Dias et al., 1992). The values reported (Coruccini and Gilbert, 1939) were later revised (Cole and Gilbert, 1951). Table 16 lists the literature values and compares them with those obtained in this research.

Liquid-phase vapor pressure measurements for *trans*-azobenzene were reported by Stull (unpublished Dow Chemical Co. measurements) (1947) and in the Engineering Sciences Data Item No. 78011 (1978). Figure 9 compares both sets of results with values obtained using the Wagner vapor-pressure equation and the parameters listed in Table 11. The deviations are large especially for values listed in Engineering Sciences Data Item No. 78011. The critical temperature listed in the Data Item, 830 K, matches that obtained in this research but the critical pressure listed, 4188 kPa, is somewhat higher than that estimated in this research, 3170 kPa.

Figure 10 compares dsc heat capacity measurements (Table 8) with values reported (Van Miltenburg and Bouwstra, 1984; Bouwstra et al., 1985). Bouwstra et al. noted "an unexpected effect" when they attempted to redetermine heat capacities for *trans*-azobenzene by "quenching" the sample and repeating the measurements. They attempted this using three samples of *trans*-azobenzene with the same results each time. The "unexpected effect" was due to freezing in disorder into the crystals during the "quenching". Although they do not state it explicitly, the enthalpy of fusion for each remeasurement was lower than that obtained during the first cycle.

Both references (Van Miltenburg and Bouwstra, 1984; Bouwstra et al., 1985) [in the latter reference the value

listed as from a first set of measurements] obtained the same enthalpy of fusion for *trans*-azobenzene, $\Delta_c^l H_m^o(C_{12}H_{10}N_2, 341.05 \text{ K}) = (22.53 \pm 0.03)$ kJ·mol^{-1} in good agreement with the value $\Delta_c^l H_m^o(C_{12}H_{10}N_2, 341.05 \text{ K}) = (23.0 \pm 0.5)$ kJ·mol^{-1} obtained in this research (Table 8).

Several determinations of enthalpies of sublimation for *trans*-azobenzene are available in the literature (Bright et al., 1950; Majury, 1956; de Kruif and van Ginkel, 1977; Schulze et al., 1977; Dias et al., 1992). Bright et al. employed a Knudsen effusion technique in the temperature range 305 to 335 K, listing the following equation to represent the measured vapor pressures in that temperature range:

$$\log(p/\text{mmHg}) = 9.721 - 3911/(T/\text{K}) \qquad (15)$$

The results listed by Bright et al. give $\Delta_c^g H_m^o(C_{12}H_{10}N_2, 320 \text{ K}) = 74.9$ kJ·mol^{-1}. The corresponding value obtained in the NIPER research was $\Delta_c^g H_m^o(C_{12}H_{10}N_2, 320 \text{ K}) = 93.4$ kJ·mol^{-1}. Majury (1956) obtained $\Delta_c^g H_m^o(C_{12}H_{10}N_2, 320 \text{ K}) = (74.1 \pm 1.7)$ kJ·mol^{-1}. Both the Bright et al. and the Majury values approach that interpolated for the enthalpy of vaporization of the *supercooled liquid trans*-azobenzene $\Delta_l^g H_m^o(C_{12}H_{10}N_2, 320 \text{ K}) = (71.2 \pm 0.6)$ kJ·mol^{-1}. Schulze et al. (1977) using ^{14}C-tracer effusion measurements obtained the following equation to represent the measured vapor pressures in the temperature region 294 to 312 K:

$$\log(p/\text{mmHg}) = (13.344 \pm 0.22) -$$
$$(4901.7 \pm 6.5)/(T/\text{K}) \quad (16)$$

The results listed by Schulze et al. give $\Delta_c^g H_m^o(C_{12}H_{10}N_2, 303 \text{ K}) = (93.84 \pm 0.12)$ kJ·mol^{-1}. de Kruif and van Ginkel (1977) using both effusion and torsion techniques obtained $\Delta_c^g H_m^o(C_{12}H_{10}N_2, 298.15 \text{ K}) = (94.93 \pm 0.84)$ kJ·mol^{-1}, $\Delta_c^g H_m^o(C_{12}H_{10}N_2, 298.15 \text{ K}) = (96.90 \pm 0.84)$ kJ·mol^{-1}, respectively. Dias et al. (1992) using an effusion technique obtained $\Delta_c^g H_m^o(C_{12}H_{10}N_2, 298.15 \text{ K}) = (93.84 \pm 0.12)$ kJ·mol^{-1}. All these values are in excellent agreement with that obtained by summing the standard enthalpies of fusion and vaporization derived in the NIPER research (Tables 8 and 13), namely $\Delta_c^g H_m^o(C_{12}H_{10}N_2, 298.15 \text{ K}) = (94.05 \pm 0.84)$ kJ·mol^{-1}.

Using the group-additivity parameters listed in (Benson, 1976; Reid et al., 1987) the ideal-gas enthalpy of formation of *trans*-azobenzene can be estimated as follows:

10	$C_b-(C_b)_2(H)$	13.82×10	138.2
2	$C_b-(C_b)_2(N_A)$	-2.1×2	-4.2
2	$N_A-(N_A)(C_b)$		
	$\Delta_f H_m^o(C_{12}H_{10}N_2, \text{g}, 298.15 \text{ K})$		134.0 kJ·mol^{-1}

The value determined in this research is $\Delta_f H_m^o(C_{12}H_{10}N_2, \text{g}, 298.15 \text{ K}) = (405.5 \pm 1.3)$ kJ·mol^{-1} (Table 14). Hence the $N_A-(N_A)(C_b)$ group parameter is derived as 135.8 kJ·mol^{-1}.

Butyl Acrylate. A search of the literature through June 1996 failed to find any thermochemical measurements other than enthalpies of polymerization (McCurdy and Laidler, 1964) on butyl acrylate. Thermophysical measurements found in the search included determinations of its vapor pressure by Stull (1947) (unpublished values from the Dow Chemical Co. files) and density values (Papayoanou and Christopulos, 1973) in the temperature range 273 to 333 K. The densities reported (Papayoanou and Christopulos, 1973) are in excellent agreement with values ($\rho_{c.s.}$) calculated using extended corresponding states (eq 11) and the parameters listed in Table 11 (see Table 17).

Liquid-phase vapor-pressure measurements for butyl acrylate reported (Stull, 1947) are compared in Figure 11
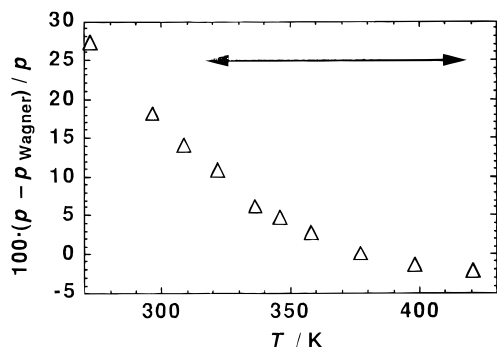
Figure 11. Comparison of literature vapor pressures for butyl acrylate with those obtained using the Wagner equation and the parameters listed in Table 11: (△) Stull (1947) The double-headed arrow represents the range of the measurements of this research and of those reported in Table 7.

with values obtained using the Wagner vapor-pressure equation and the parameters listed in Table 11. Above 340 K agreement is within the probable uncertainty interval in the Dow measurements.

Addition of the group-additivity parameters from Benson (1976) and Reid et al. (1987) plus the O−(CO)(C) group parameter derived in Steele et al. (1991a, 1994b) to estimate the enthalpy of formation of butyl acrylate follows:

1	$C_d-(C_d)(H)_2$	26.21×1	26.21
1	$C_d-(C_d)(CO)(H)$	35.59×1	35.59
1	$CO-(C_d)(O)$	-136.1×1	−136.1
1	$O-(CO)(C)$	-179.7×1	−179.7
1	$C-(O)(C)(H)_2$	-33.91×1	−33.91
2	$C-(C)_2(H)_2$	-20.72×2	−41.44
1	$C-(C)(H)_3$	-42.25×1	−42.25
	$\Delta_f H_m^\circ(C_7H_{12}O_2$, g, 298.15 K)		−371.8 kJ·mol⁻¹

The value determined in this research is $\Delta_f H_m^\circ(C_7H_{12}O_2$, g, 298.15 K) = −(375.3 ± 0.8) kJ·mol⁻¹ (Table 14).

Eigenmann, Golden, and Benson (1973) in their revision of the group-additivity parameters for oxygen-containing compounds list 20.9 kJ for the $C_d-(C_d)(CO)(H)$ parameter and −133.9 kJ for the $CO-(C_d)(O)$ parameter. Using those parameters gives $\Delta_f H_m^\circ(C_7H_{12}O_2$, g, 298.15 K) = −384.1 kJ·mol⁻¹. Obviously, the revised parameters give a *larger* absolute deviation from the experimentally determined value for the ideal-gas enthalpy of formation.

In the 1990 871 project (Steele et al., 1994b) an ideal-gas enthalpy of formation for dibutyl fumarate, $\Delta_f H_m^\circ$-(C₁₂H₂₀O₄, g, 298.15 K) = −795.5 kJ·mol⁻¹, was derived using the parameters from Benson (1976) and Reid et al. (1987). That was compared with an experimentally determined value of $\Delta_f H_m^\circ(C_{12}H_{20}O_4$, g, 298.15 K) = −(802.0 ± 5.0) kJ·mol⁻¹. Using the Eigenmann et al. (1973) revised parameters would shift the estimated value to −820.5 kJ·mol⁻¹.

Using both of the experimentally determined values [butyl acrylate and dibutyl fumarate (Steele et al., 1994b)] the sum of the group parameters is derived as

$$C_d-(C_d)(CO)(H) + CO-(C_d)(O) = -104.0 \text{ kJ·mol}^{-1}$$

Either one or both of the parameters need slight revision from the values given in Benson (1976) and Reid et al. (1987) [the sum of both values is −100.5 kJ]. The revised group parameter values listed in Eigenmann et al. (1973) are in error [the sum of both values is −113 kJ]. Additional enthalpy of formation measurements on compounds which contain *one* but *not both* groups would be beneficial in resolving the discrepancies which still exist.

Di-tert-butyl Ether. Only sufficient di-*tert*-butyl ether was available for the combustion calorimetric measure-

ments. Two previous determinations of the enthalpy of combustion of di-*tert*-butyl ether were found in a search of the literature through June 1993. Smutny and Bondi (1961) reported $\Delta_c H_m^\circ(_8H_{18}O$, l) = −(5308.2 ± 1.0) kJ·mol⁻¹. Later, Fenwick et al. (1975) obtained $\Delta_c H_m^\circ(C_8H_{18}O$, l) = −(5320.95 ± 1.08) kJ·mol⁻¹. The enthalpy of combustion obtained in this research (Table 6) was $\Delta_c H_m^\circ(C_8H_{18}O$, l) = −(5322.1 ± 0.61) kJ·mol⁻¹ in good agreement with the NPL (National Physical Laboratory, Teddington, England) value (Fenwick et al., 1975).

The good agreement between the combustion calorimetric values obtained at NPL and at NIPER lends weight to their other measurements on di-*tert*-butyl ether. The vapor pressure measurements for di-*tert*-butyl ether reported (Ambrose et al., 1976) were used to derive the ideal-gas enthalpy of formation at 298.15 K. Derived enthalpies of vaporization (Tables 13 and 14) agree within the stated uncertainty intervals with those derived (Ambrose et al., 1976) or measured (Fenwick et al., 1975) using a vaporization calorimeter.

Densities reported (Smutny and Bondi, 1961; Obama et al., 1985) are in excellent agreement with values ($\rho_{c.s.}$) calculated using extended corresponding states (eq 11) and the parameters listed in Table 11 (see Table 17). However, the density reported by Fenwick et al. in their paper on the combustion calorimetry of di-*tert*-butyl ether is 0.4% higher than that obtained both in the NIPER research and by Obama et al. (1985).

Addition of the group-additivity parameters from Benson (1976) and Reid et al. (1987) to estimate the enthalpy of formation of di-tert-butyl ether follows:

6	$C-(C)(H)_3$	-42.25×6	−253.50
2	$C-(C)_3(O)$	-27.63×2	−55.26
1	$O-(C)_2$	-99.23×1	−99.23
1	strain		
	$\Delta_f H_m^\circ(C_8H_{18}O$, g, 298.15 K)		−407.99 kJ·mol⁻¹

The value determined in this research is $\Delta_f H_m^\circ(C_8H_{18}O$, g, 298.15 K) = −(361.1 ± 0.8) kJ·mol⁻¹ (Table 14). Hence, the strain parameter in di-*tert*-butyl ether is 46.9 kJ.

As noted above in the discussion of the results for 1,2-dimethoxyethane, in unpublished work at NIPER the $O-(C)_2$ group was assigned a value of −97.07 kJ·mol⁻¹. That change would give a strain parameter in di-*tert*-butyl ether of 44.7 kJ. As noted in the 1,2-dimethoxyethane section, further measurements on dialkyl ethers are required to resolve the discrepancies that still exist.

Hexane-1,6-diol. In the 1989 results (Steele et al., 1991b), the ideal-gas standard enthalpy of formation of hexane-1,6-diol derived from the experimental results was shown to be 7 kJ·mol⁻¹ more positive than that estimated using the group-additivity parameters:

2	$C-(C)(O)(H)_2$	-33.91×2	−67.82
2	$O-(C)(H)$	-158.68×2	−317.36
4	$C-(C)_2(H)_2$	-20.21×4	−80.84
	$\Delta_f H_m^\circ(C_6H_{14}O_2$, g, 298.15 K)		−466.02 kJ·mol⁻¹

using the $C(C)_2(H)_2$ group-additivity parameter derived for the alkanols in the 1989 871 report (Steele et al., 1991b).

In communications (Syverud, 1991) with one of the authors of this report, Dr. Alan N. Syverud questioned the validity of the long extrapolations of the vapor pressures necessary to derive enthalpies of vaporization for the supercooled diols [hexane-1,6-diol (Steele et al., 1991b) and decane-1,10-diol (Steele et al., 1994b)]. Dr. Syverud noted that ideal-gas heat capacities derived from the results appeared "quite accurate" within the vapor-pressure range but became abnormally small at lower temperatures.

Past experience within the Thermodynamics Group at NIPER has shown that long extrapolations of this type can,

under certain circumstances, be prone to large errors ($\pm$10%) in the derived enthalpies of vaporization. This is due to the fact that the derivation of an enthalpy of vaporization requires an accurate knowledge of the *slope* of the vapor pressure versus temperature curve in the requisite temperature region.

To help resolve the discrepancies, inclined-piston vapor-pressure measurements were made on hexane-1,6-diol. The results are listed in Table 7.

It should be noted that the inclined-piston results are not completely consistent with the previously determined ebulliometric data (Steele et al., 1991b) with differences of approximately 2 Pa in the overlap region. In addition, the Wagner equation parameters (Table 11) derived from the fitting procedures appear "odd". That may be due to either a wrong critical temperature or a critical pressure which is too high. However, although the parameters may be completely fictitious the extrapolation to low temperatures should not be unduly affected by them. (The use of the fitting parameters to estimate vapor pressures above the upper temperature bound of the experimental measurements is not recommended.)

Table 13 lists the derived enthalpies of vaporization for hexane-1,6-diol including the inclined-piston vapor pressure results. Table 14 gives the corresponding enthalpies of formation.

The ideal-gas enthalpy of formation at 298.15 K determined in this research is $\Delta_f H_m^o$(C$_6$H$_{14}$O$_2$, g, 298.15 K) = $-$(463.8 $\pm$ 2.2) kJ$\cdot$mol^{-1} (Table 14). Agreement with that derived by summation of the group parameters ($-$466.0 kJ$\cdot$mol^{-1} see above) is within the assigned experimental uncertainty interval. The previous discrepancy was due to a wrong 124 K extrapolation of the ebulliometric vapor pressure measurements.

Conclusions

Revised or New Groups. The C$_d$$-$(C$_d$)(O)(H) and O$-$(C$_d$)(C) group-additivity parameter values were confirmed by the excellent agreement between estimated and determined values for the ideal-gas enthalpy of formation of butyl vinyl ether. The 1,2-dimethoxyethane result leads to reassigning the O$-$(C)$_2$ group additivity parameter value as $-$97.07 kJ$\cdot$mol^{-1} from the previous value of $-$99.23 kJ$\cdot$mol^{-1}. A 1,4-(O,O)-interaction energy of $+$4 kJ$\cdot$mol^{-1} was tentatively assigned. The C$-$(O)(CO)(H)$_2$ group additivity parameter value $-$29.2 kJ$\cdot$mol^{-1} was derived. A strain energy term of 84.9 kJ$\cdot$mol^{-1} was derived for bicyclo-[2.2.1]hept-2-ene ring systems. A definitive enthalpy of formation for bicyclo[2.2.1]hept-2-ene $\Delta_f H_m^o$(C$_7$H$_{10}$, c, 298.15 K) = (44.44 $\pm$ 2.00) kJ$\cdot$mol^{-1} was determined, resolving earlier discrepancies in the experimentally determined values. The N$_A$$-$(N$_A$)(C$_b$) group-additivity parameter value 135.8 kJ$\cdot$mol^{-1} was derived. The results for butyl acrylate define the sum of the C$_d$$-$(C$_d$)(CO)(H) and CO$-$(C$_d$)(O) as $-$104.0 kJ$\cdot$mol^{-1}. Earlier values for the sum of those two groups were $-$100.5 and $-$113 kJ$\cdot$mol^{-1} in Reid et al. (1987) and Eigenmann et al. (1973), respectively. Additional enthalpy of formation measurements on compounds which contain *one* but *not both* groups would be beneficial in resolving the discrepancies which still exist. A strain energy term for di-*tert*-butyl ether of 44.7 kJ$\cdot$mol^{-1} was derived using the reassessed O$-$(C)$_2$ group-additivity parameter value $-$97.07 kJ$\cdot$mol^{-1}. The ideal-gas enthalpy of formation of hexane-1,6-diol, $\Delta_f H_m^o$(C$_6$H$_{14}$O$_2$, g, 298.15 K) = $-$(463.8 $\pm$ 2.2) kJ$\cdot$mol^{-1}, was determined by resolving earlier discrepancies between the experimentally determined value and that obtained by summation of group-additivity parameters.

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