Thermochemistry of Eight Membered Ring Hydrocarbons. The Enthalpy of Formation of Cyclooctane

DANIELA GHEORGHE[1]*, ANA NEACSU[1], STEFAN PERISANU[2]
[1]Ilie Murgulescu Institute of Physical Chemistry of the Romanian Academy, 202 Splaiul Independentei, 060021, Bucharest, Romania
[2] Politehnica University of Bucharest , Department of General Chemistry, 1 Polizu Str., 011061, Bucharest, Romania

Abstract: *A new value of the enthalpy of formation of cyclooctane (-156.2±1.2 kJ mol^{-1}) based on heat of combustion measurements is reported. Its solid - liquid phase change was investigated by differential scanning calorimetry in both directions revealing an overcooling effect of over 23 K. Our enthalpy of formation of cyclooctane was used together with literature values of heats of hydrogenation of 8 carbon atoms cycloolefins to calculate the enthalpies of formation of the later. The strain energies of the investigated molecules were calculated and discussed.*

Keywords: *cyclooctane; enthalpy of formation; strain energies; differential scanning calorimetry (DSC); overcooling.*

1. Introduction

The literature value for the enthalpy of formation of cyclooctane, selected and reanalyzed by Cox and Pilcher [1] (i.e. $\Delta_f H^o_{liq}$= -169.4±1.6 kJ mol^{-1}) is based on the enthalpy of combustion measured by Spitzer and Huffman in 1947 [2] ($\Delta_c H^°_{liq}$= -5265.7±0.9 kJ mol^{-1}). A relatively more recent determination comes from Kaarsemaker and Coops [3] in 1952 whose value yields $\Delta_f H^o_{liq}$ = -169.0 kJ mol^{-1}. The values from both references agree within the error limits as well as with that from DIPPR 801 project [4] (-167.74 kJ mol^{-1}). An even older value of the enthalpy of combustion was reported by Ruzieka and Schlapfer in 1933 for the solid state [5]. Their value was used by NIST [6] to obtain $\Delta_f H^o_{solid}$= -182 kJ mol^{-1}. Enthalpies of formation of unstrained alkanes were calculated by Zavitsas et al. [7, 8] based on the number of different kinds of hydrogen atoms. The enthalpy of formation of cyclooctane is not important only for the study of the energetics of this molecule, but also of that of all eight membered ring cycloalkenes, whose enthalpies of formation are derived from enthalpies of hydrogenation to cyclooctane.

2. Materials and methods
2.1. Materials

The cyclooctane used was a product of Aldrich (CAS No. 292-64-8, purity >99%). The liquid samples were dried and stored over 4 Å molecular sieves and used without further purification. Evidence of chemical purity is also provided by comparison of measured physical properties, which are in good agreement with literature values, as it can be seen in Table 1. The molecular weights of the compounds were calculated using values recommended by the IUPAC Commission, in 2011 [9], for the atomic weights of their constituent chemical elements.

Apparatus and experimental procedures
Refractive indices and density

Measurements of the refractive index of cyclooctane were carried out at sodium D-line, λ_D = 589.3 nm, using a digital automatic refractometer (Anton Paar RXA 170) with an accuracy of ±0.01 K in temperature and of ±0.000001 for refractive index.

*email:gheorghedanny2@gmail.com

The density measurements at 298.15 K for cyclooctane were carried out by using a density and sound velocity meter Anton Paar DSA-5000 M with an accuracy of ±0.05 kg m^{-3}. Dried air and deionized ultra-pure water at atmospheric pressure were used as calibration fluids. The sample temperature was maintained constant within ±0.01 K. The experimental data for refractive index and density at T= 298.15 K are shown in Table 1.

Table 1. Physical properties of cyclooctane at
T= 298.15 K and P^o= 0.1 MPa

Properties	$n_D^{298.15\ K}$	$10^{-3} \cdot \rho / kg \cdot m^{-3}$
Experimental	1.455897	0.831546
Literature	1.45598 [10] 1.4560 [11]	0.83147 [10] 0.83151 [11]

2.2.2. Combustion calorimetry

A Parr Instruments model 6200 microprocessor controlled isoperibol oxygen bomb calorimeter was used in combustion experiments. Temperature is measured with a high precision electronic thermometer using a specially designed thermistor sensor. Measurements were taken with 0.0001 K resolution. The jacket temperature is held constant for isoperibol operation. A microprocessor-based controller monitors both the temperatures of the bucket and of the jacket and performs the necessary heat leak corrections that result from differences between these two temperatures. These corrections are applied continuously throughout a test rather than as a final correction based on pre and post test measurements.

The combustion calorimeter was calibrated by means of ten combustion experiments with benzoic acid (CAS 65-85-0) supplied by Parr Company, having the massic energy of combustion under certificate conditions ($\Delta_c u^o$ = -26434.5 J g^{-1}). The energy equivalent of our calorimeter was determined as ε_{calor}= (10054.4±1.4) J K^{-1}. The uncertainty associated with the average value of the energy equivalent is the standard deviation of mean.

The combustion bomb Parr Instruments standard type 1108 is a cylinder, with an internal volume of about 0.35 L, made of stainless steel, as well as its accessories. The samples burned in the oxygen filled bomb were enclosed in Parr 3601 Gelatin Capsules with maximum 0.9 mL volume. A cotton thread was used in order to ignite the samples. The completely equipped bomb (filament, fuse, gelatin capsule, sample, deionized water) was connected to the oxygen cylinder and flushed with oxygen. All combustion experiments were carried out in high purity oxygen 99.998% at 3.546 MPa and at T = 298.15 K and in the presence of 1 cm^3 of deionized water for saturation of the atmosphere.

2.2.3. Differential scanning calorimetry

A Perkin Elmer power compensated DSC (model 8500) was used for the measurement of the enthalpies of the processes occurring during temperature scan (fusion and crystallization). The calorimeter was calibrated with high purity indium (T_m= 429.75 K and $\Delta_{fus}H$ = 28.46 J g^{-1}). The areas of the peaks corresponding to the standard and studied samples were used to calibrate the instrument and calculate the thermal effects for cyclooctane. Aluminum sealed pans were used. The DSC experiments were done at a heating rate of 10 K min^{-1} using nitrogen with purity > 99.996% (flux 20 mL min^{-1}). The heat flow curves were processed by means of Pyris Software, which delivered the thermal effects and the purity.

3. Results and discussions

3.1. Combustion energy

The data of the combustion measurements for cyclooctane are given in Table 2. Samples amounting between 0.1–0.4 g and gelatin capsules with a mass of 0.10–0.12 g were used in each experiment. The samples were weighed with a Mettler-Toledo microbalance with an accuracy of

$\pm 2 \cdot 10^{-6}$ g. Some runs were rejected because of doubt about combustion completeness. The corrections for the gelatin capsule, the cotton thread and filament used in the combustion experiments were calculated from the corresponding masses and energies of combustion. $\Delta_c u^\circ_{(gelatin\ capsule)} = 19294 \pm 3$ J g^{-1} was determined in our laboratory (to be compared with the value certified by the fabricant 19.26 kJ g^{-1}), $\Delta_c u^\circ_{(cotton)} = 16709 \pm 5$ J g^{-1} checked in our laboratory in agrrement with literature value 16240 J g^{-1} [12] and $\Delta_c u^\circ_{(Ni–Cr)} = 5.86$ kJ g^{-1} (certified by the calorimeter's fabricant). In order to bring the experimental values of the energy of combustion to the standard state ($T = 298.15$ K and $P^\circ = 0.1$ MPa), corrections were made with the Washburn approximate equation [13]:

$$\Pi\% = \frac{-0.3 \cdot a \cdot P_{initial}}{-\Delta U^{exp}} \left[1 - \frac{1.1 \cdot (b\text{-}2 \cdot c)}{4 \cdot a} + \frac{2}{P_{initial}} \right] \qquad (1)$$
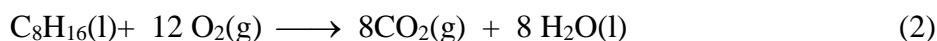
where: P stands for the initial oxygen pressure and $-\Delta U^{exp}$ for the experimental energy of combustion; a, b, and c are the numbers of carbon, hydrogen and oxygen atoms from the chemical formula of the compound, $C_a H_b$. The Washburn correction Π is calculated in percents from the experimental value.

Table 2. Results for typical combustion experiments at
$T = 298.15$ K and $P^\circ = 0.1$ MPa for cyclooctane liquid *

Sample	1	2	3	4	5	6	7
m_{sample}/g	0.340047	0.282063	0.197046	0.213378	0.273059	0.258980	0.207492
$m_{capsule}$/g	0.113303	0.115819	0.111027	0.114851	0.113728	0.11626	0.110691
$m_{(Ni–Cr)}$/g	0.007585	0.008269	0.000005	0.00622	0.002811	0.00542	0.003892
m_{cotton}/g	0.009182	0.008555	0.008589	0.007849	0.007883	0.009052	0.010031
ΔT/K	1.8267	1.5598	1.1483	1.2345	1.5095	1.4516	1.2009
$\varepsilon_{calor}(-\Delta T_c)$/J	-18366.36	-15682.85	-11545.46	-12412.15	-15177.11	-14594.96	-12074.32
- $m_{capsule}\Delta_c u^\circ_{capsule}$/J	-2186.09	-2234.63	-2142.18	-2215.96	-2194.29	-2243.14	-2135.69
-$m_{wire}\Delta_c u^\circ_{wire}$/J	-44.43	-48.44	-0.03	-36.43	-16.47	-31.75	-22.8
-$m_{cotton}\Delta_c u^\circ_{cotton}$/J	-153.42	-142.95	-143.51	-131.15	-131.72	-151.25	-167.61
-$\Delta_c u$ /Jg^{-1}	-47000.6	-46999.5	-46992.8	-46999.3	-47003.2	-46987.5	-46981.2
-$\Delta_c u^\circ$/Jg^{-1}	-46958.0	-46956.9	-46950.2	-46956.7	-46960.6	-46944.9	-46938.6
<$\Delta_c u^\circ$>/ Jg^{-1}	-(46952.3±8.1)						

* m_{sample} – mass of compound burned in each experiment; $m_{capsule}$ – mass of gelatin capsule burned in each experiment; $m_{(Ni–Cr)}$ – mass of fire burned in each experiment; m_{cotton} – mass of cotton burned in each experiment; ΔT – temperature rise; ε_{calor} – the energy equivalent of the calorimeter; Δu_{cotton} – energy of combustion of the cotton fuse; Δu_{ign} – energy used to ignite the sample by means of a fire; $\Delta_c u$ – non-corrected massic energy of combustion of compound; $\Delta_c u^\circ$ – standard energy of combustion; <$\Delta_c u^\circ$> – mean value of standard massic energy of combustion; $u(\Delta_c u^\circ)$ – uncertainties in this table are expressed as the standard deviation of the mean.

The standard combustion enthalpy $\Delta_c H^\circ$ of cyclooctane was calculated taking into account the following reaction:

$$C_8 H_{16}(l) + 12\ O_2(g) \longrightarrow 8 CO_2(g) + 8\ H_2O(l) \qquad (2)$$

by using the equation:

$$\Delta_c H^\circ = \Delta_c U^\circ + \Delta n RT \qquad (3)$$

where Δn is the change in the mole number of gaseous compounds during the combustion reaction:

$$\Delta n = \Sigma n_{products,g} - \Sigma n_{reactants,g} \qquad (4)$$

As recommended by Olofsson [14], the uncertainty associated with the molar enthalpy of combustion is twice the overall standard deviation of the mean, and it includes the uncertainties

associated with the calibration experiments (uncertainties of massic energy of combustion of benzoic acid and energetic equivalent of the calorimeter) and with the auxiliary materials.

The following values were considered: $\Delta_f H^o_{CO2(g)}= -393.51\pm0.13$ kJ mol^{-1}, $\Delta_f H^o_{H2O(l)}= -285.83\pm0.042$ kJ mol^{-1} [15] for calculating the enthalpy of formation,. The obtained value of the standard molar enthalpy of formation in liquid-state is shown in Table 3, together with literature [1, 4, 6] and calculated values [16].
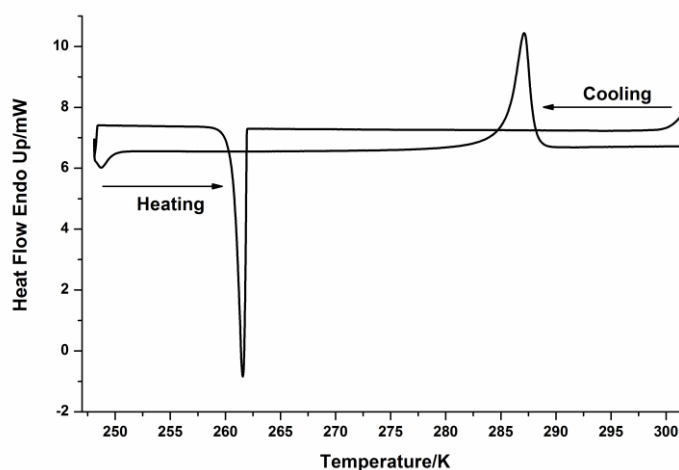
Table 3. Thermochemical data at $T= 298.15$ K and $P^o= 0.1$ MPa for liquid cyclooctane

$-\Delta_c U^o$/kJ mol^{-1}	$-\Delta_c H^o$/kJ mol^{-1}	$-\Delta_t H^o$/kJ mol^{-1} (this work)∗	$-\Delta_t H^o$/kJ mol^{-1} (literature)	$-\Delta_t H^o$/kJ mol^{-1} (calculated)
5268.5±1.1	5278.4±1.1	156.2±1.2	169.4±1.6 [1] 169.0 (no Washburn corrections) [3] 167.74 [4]	205.84 [16] (strainless)

∗Uncertainty is standard deviations and includes the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2.

3.2. DSC runs

The purity of liquid cyclooctane could be estimated from the DSC curve, based on the shape and the temperature of the DSC melting endotherm, as is shown in Figure. 1.

Figure 1. DSC curve of cyclooctane

Table 4. Thermochemical parameters of cyclooctane
derived from DSC measurements

Process	$T_{on\ set}$/K	T_{max}/ K	$T_{end\ set}$/ K	$\Delta H_{Process}$ /kJ mol^{-1}
crystallization	-261.93	-261.58	-260.7	-1.92
melting	285.45	287.12	288.06	2.28

Our value of the melting temperature of 285.5 K fairly agrees with the range indicated by NIST [17] (285 ± 5 K) or by reference [18] (286 K) but not with that recommended by the CRC Handbook (288 K) [19]. So does our value for the enthalpy of fusion (2.28 kJ mol^{-1}) if compared with that reported by Acree and Chickos [20] (2.41 kJ mol^{-1}). However these values are very far from that estimated by means of the method of Chickos et al. [21], i.e. 16.25 kJ mol^{-1}. This discrepancy can be explained as follows: the estimation method yields the enthalpy change between the liquid state and the crystalline state corresponding to 0 K, while the experimental value corresponds to a solid structure

much more similar to that of the liquid. This explanation is consistent with the value of the enthalpy of sublimation reported by Bondi [22] at 166 K, 58.7 kJ mol^{-1}.

An important overcooling effect, of over 23 K is observed. The crystallization enthalpy of the overcooled liquid corresponding to a nonequilibrium process is lower in absolute value than that of equilibrium melting.

3.3. Determination of purity by DSC

The Perkin Elmer Pyris DSC purity analysis software permits the assessment of purities for samples which undergo simultaneous degradation during melting. In Figure 2 is plotted the purity using Pyris software for cyclooctane. In the T vs. $1/F_S$ curve, the corrected data points are shown as black circles and the line drawn through them shows how the data fit the van't Hoff relationship Eq. (5). The black boxes represent the uncorrected values calculated for $1/F_S$ (fraction melted) at given temperatures (Figure 3).

$$1/F_S = [\Delta H/R] \cdot [T_0 - T_S]/T_0^2 \cdot [1/X_2] \qquad (5)$$

T_S-sample temperature and the melting temperature, K;
T_0-the melting temperature of the pure substance;
ΔH-heat of melting of the pure material, J/g;
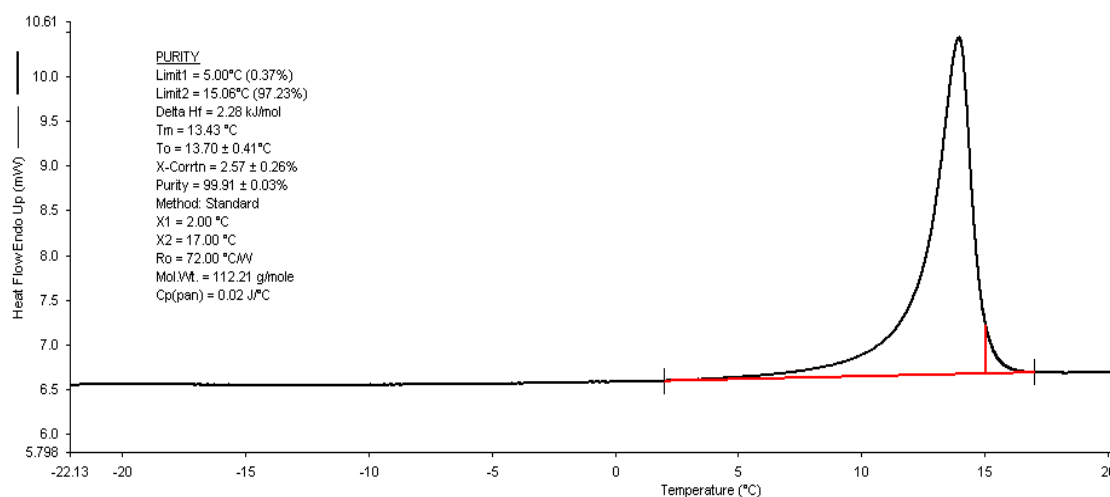X_2-mole fraction of impurity in the sample;
R-constant (8.314 J/mol K);
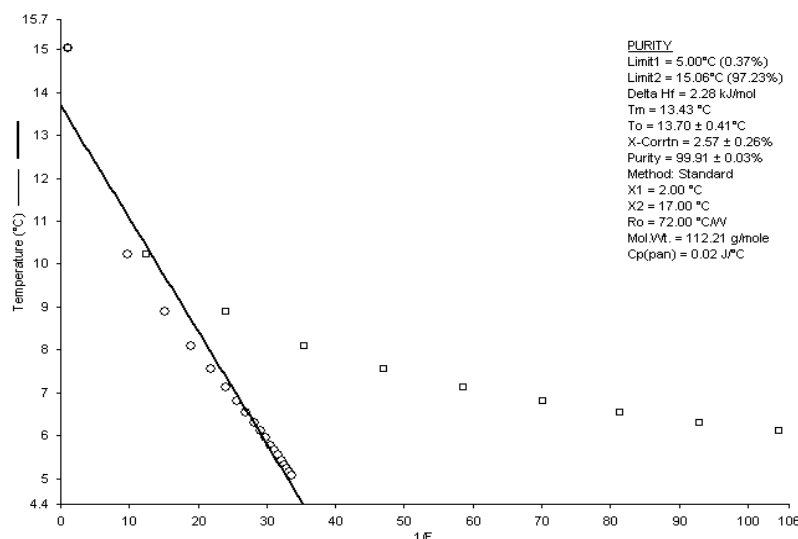F_S-fraction of sample melting at temperature T_S;
$F_S = A_S/A_t$
A_S-area of the melting endotherm up to temperature T_S;
A_t-total area of melting endotherm

The DSC results indicated a higher purity 99.91±0.03% than the certified purity >99% (GC) from Aldrich (CAS No. 292-64-8).

Figure 2. Determination of purity using Pyris software for cyclooctane

Figure 3. van't Hoff plot for cyclooctane

Our value of the enthalpy of formation in liquid state (-156.2±1.2 kJ mol^{-1}) is less negative than literature data. This value corresponds to very large ring strain energy, of 49.6 kJ mol^{-1}, if the group additivity scheme is used [16]. This value is closer to those of cyclononane and cyclodecane that to that of cycloheptane.

Different literature sources [3, 23] report for the standard enthalpy of vaporization values between 43.3 and 44.7 kJ mol^{-1}. We obtain a value of -112.8 kJ mol^{-1} for the ideal gas state enthalpy of formation, corresponding to a ring strain of over 52 kJ mol^{-1}. Strain energies for cyclooctane ranging between 40 and 50 kJ mol^{-1} were reported in literature according to Zavitsas et al. [8] and of almost 60 kJ mol^{-1} by Rogers et al. [26].

For the solid state enthalpy of formation of cyclooctane a value of -182 kJ mol^{-1} was reported by Ruzieka and Schlapfer [5]. The calculated value in this state is -235.28 kJ mol^{-1} [16] and -238.4 kJ mol^{-1} [24]. A ring strain of 55 ± 3 kJ mol^{-1} is resulting from these data. The very low experimental value of the heat of fusion does not allow us to evaluate a ring strain in this state.

Most values of enthalpies of formation of eight membered ring cycloalkenes come from heats of hydrogenation and are based on the value of the enthalpy of formation of cyclooctane. In Table 5 are listed the experimental and calculated enthalpies of formation of such molecules, together with the corresponding strain energy.

The case of cyclooctene was more thoroughly investigated. The values of $\Delta_f H°$ of the cis isomer of this compound are calculated by means of heats of hydrogenation ranging between -96 and -103 kJ mol^{-1}. [25-28] The resulting strain of this molecule in liquid state (32-39 kJ mol^{-1}) is to be compared with the gas phase values resulting from data of authors [25, 26, 30] i.e. between 24 and 43 kJ mol^{-1}. It is considered that cyclooctane contains considerable strain from van der Waals repulsion and unfavorable torsion, which is partly relieved in cis-cyclooctene. The much larger strain energy of trans-cyclooctene (71 - 93 kJ mol^{-1}) is consistent with the instability of trans isomers of cycloalkenes with less than 10 atoms.

Table 5. Liquid phase enthalpies of hydrogenation and formation of 8-membered
ring cycloalkenes and the corresponding strain energies

Molecule	-$\Delta_h H°$/ kJ mol^{-1}	$\Delta_f H°$(exp) /kJ mol^{-1}	$\Delta_f H°$(calcd)/ kJ mol^{-1} [16]	Strain energy/ kJ mol^{-1}
cis-cyclooctene	102 [25] 96.4 [26] 103 [27] 96.1[28]	-53 — -60	-92.28	32 - 39

trans-cyclooctene	144 [26] 135 [28] 144 [31]	-12 — -21	-92.28	71 - 80
cyclooctene unspecified stereoisomer	94 [29]	-62	-92.28	30
1, 3-cyclooctadiene, (Z,Z)-	204.8 [31] 208 [35]	49 — 52	3.54	45 - 49
1,3-cyclooctadiene, (E,Z)-	271 [31]	115	3.54	111
1,4-cyclooctadiene, unspecified stereoisomer	217.9 [28]	62	22.67	39
1,5-cyclooctadiene, (E,E)-	320 [31]	164	21.28	143
1,5-cyclooctadiene, (E,Z)-	282 [31]	126	21.28	105
1,5-cyclooctadiene, unspecified stereoisomer	230 [31] 224.6 [35]	69 — 74	21.28	48 - 53
1, 3, 5-cyclooctatriene	319.6 [35] 302.8 [28]	146.5 — 163.5	99.36	47 - 64
1, 3, 6-cyclooctatriene	343.3 [35]	187	119.7	67
cyclooctatetraene	409.9 [28]	254	177.44	75

Although the most stable cyclooctadiene isomer is observed to be 1, 3-cyclooctadiene, (Z,Z)- a high value of strain energy is calculated for it. In fact this comes partially from a lack of conjugation of the two double bonds, conjugation taken into account in the calculated value. For 1,5-cyclooctadiene, three values of the enthalpy of formation based on heats of combustion were reported too [32-34]. The first two are assigned to the -ZZ stereoisomer, while for the last it is not specified. The last two values of $\Delta_f H^o$, 18 kJ mol^{-1} [33] and 24 kJ mol^{-1} [34] would correspond to an improbable quasi-zero ring strain, while the value of authors [32] (57.7 kJ mol^{-1}) is over 10 kJ mol^{-1} lower than the value obtained from heats of hydrogenation.

The isomer with conjugated structure is again the most stable in the case of cyclooctatrienes. It is observed that for samples of unspecified stereoisomers the enthalpy of hydrogenation has usually less negative values. This is probably due to a mixing effect.

An important value of the strain energy (75 kJ mol^{-1}) is calculated for cyclooctatetraene. As in the case of the other conjugated molecules, the calculated value of $\Delta_f H^o$ includes a cconjugative stabilization contribution (group parameter [C_d- C_dH]) [16]. In fact in such a non-planar molecule such a contribution should be largely suppressed. [28, 35, 36] Two values of $\Delta_f H^o$(l) obtained from heats of combustion are available 254.5 kJ mol^{-1} [37] and 248 kJ mol^{-1} [38]. The agreement between this first value and that calculated by us is excellent.

4. Conclusions

The ring strain energy of cyclooctane is quite large which explains the difficulty of synthesizing compounds with 8-membered rings.

The thermodynamic parameters of melting indicate that premelting processes occur at lower temperatures.

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