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The enthalpy of sublimation of cubane

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This paper is dedicated to Philip E. Eaton and Thomas W. Cole, Jr. on the occasion of the 40th anniversary
of the first successful synthesis of cubane and any of its derivatives

Abstract

The sublimation enthalpy of cubane, a key reference material for force field and quantum mechanical computations, was measured by combining the vaporization enthalpy at $T = 298.15\,\mathrm{K}$ to the sum of the fusion enthalpy measured at $T = 405\,\mathrm{K}$ and a solid–solid phase transition that occurs at $T = 394\,\mathrm{K}$. The fusion and solid–solid phase transitions were measured previously. A sublimation enthalpy value of $(55.2 \pm 2.0)\,\mathrm{kJ\,mol^{-1}}$ at $T = 298.15\,\mathrm{K}$ was obtained. This value compares quite favorably the value obtained by comparing the sublimation enthalpy of similar substances as a function of their molar masses but is at odds with earlier measurements.

Keywords: Cubane; Hydrocarbons; Vaporization; Sublimation; Phase change; Enthalpy

1. Introduction

This is the 40th anniversary of the first successful synthesis of the polycyclic hydrocarbon cubane [1]: two other syntheses soon followed [2]. As befits the high symmetry and accompanying esthetics, large strain energy and thus high energy, and eight tertiary carbons all capable of possible functionalization, the chemistry of this seemingly simple 8-carbon hydrocarbon and its derivatives has blossomed as evidenced by numerous reviews in which it is featured prominently [3]. The eponymic (i.e., cubical) symmetry of cubane results in there being a single type of carbon environment and of bonded hydrogen, one type of C–C and C–H bond and associated bond lengths, and one unique C–C–C and C–C–H angle. Very few hydrocarbons have such a minimal description[1]. Accordingly, paralleling the "organic" chemistry (and related bio- and high energy chemistry) interest in cubane and its derivatives, the physical chemists have been active—soon after the first synthesis of cubane itself there was a measurement of the enthalpies of combustion and of sublimation of this hydrocarbon [4] from which the gas phase enthalpy of formation of $622.2 \pm 4.2\,\mathrm{kJ\,mol^{-1}}$ was derived. In turn, this quantity and the molecular high symmetry have meant that molecular mechanicians have been active: for example, cubane has been important in the development of the recent molecular mechanical model, MM4 [5a] and its predecessor, MM3 [5b] and quantum chemists have likewise been active with high level methodologies [6a,b]. Calculations at the G2(MP2) level give 606.7 or $625.9\,\mathrm{kJ\,mol^{-1}}$ depending on whether the atomization or bond separation method is used [6a], while the G3(MP2) result is $610.9\,\mathrm{kJ\,mol^{-1}}$, $11.3\,\mathrm{kJ\,mol^{-1}}$ lower than the reported experimental value [6b,c].

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[1] The other known minimal hydrocarbons are methane, ethane, ethylene, acetylene, cyclopropane, neopentane, benzene, and dodecahedrane. Cyclohexane and cyclobutane, for example, do not qualify because there is a difference between equatorial and axial hydrogens; allene does not qualify because of two types of carbon, and cyclooctatetraene does not qualify because of two different types of carbon–carbon bonds. Ideally, diamond, graphite and polyethylene would qualify, however, there are end effects arising from the finiteness of the sample.

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Recently using an analysis based on the sublimation enthalpies of other cyclic and polycyclic hydrocarbons, it has been suggested that the enthalpy of sublimation of cubane is seriously in error [7]. This raises considerable concern as to the enthalpy of formation of gaseous cubane and all related analyses. We recall that there is some controversy about the enthalpy of combustion, and thus formation of its 1,4-dicarbomethoxy derivative [8]. The current study reports a new experimental determination of the enthalpy of sublimation of cubane. Let us summarize our findings and analyses that follow: the just enunciated literature suggestion is verified and the derived concern is justified.

2. Experimental

All standards were purchased from the Aldrich Chemical Company and were used without any further purification. Each was analyzed by gas chromatography and found to be at least 99 mole percent pure. Cubane (+99 mol%) was kindly supplied by Professor Phillip Eaton. Correlation gas chromatography experiments were performed on an HP 5890A Series II Gas Chromatograph equipped with a split/splitless capillary injection port and a flame ionization detector run at a split ratio of 100/1. Retention times were recorded to three significant figures following the decimal point on a HP 3989A Integrator. The instrument was

Table 1
Cubane mixture

Retention times	t_r (min)						
(A) Mixture 1							
T/K		348.7	353.9	358.9	364	369.1	374.2
Methane[a]		1.328	1.349	1.353	1.373	1.341	1.359
Nonane		3.87	3.105	2.826	2.621	2.449	2.312
Cubane		5.485	4.25	3.799	3.453	3.168	2.935
Decane		6.964	5.081	4.437	3.927	3.524	3.199
exo-THDCPD[b]		10.105	7.271	6.286	5.495	4.865	4.35
Undecane		13.53	9.102	7.645	6.488	5.594	4.88
endo-THDCPD[b]		12.247	8.658	7.404	6.488	5.645	4.993
(B) Mixture 2							
T/K	343.6	348.6	353.8	358.8	363.9	368.9	374
Methane[a]	1.27	1.283	1.29	1.342	1.344	1.357	1.375
Norbornene	1.957	1.879	1.809	1.76	1.71	1.68	1.665
Octane	2.481	2.302	2.154	2.04	1.947	1.875	1.83
Cubane	5.472	4.779	4.215	3.77	3.4	3.113	2.895
Adamantane	11.43	9.585	8.124	6.967	6.049	5.315	4.929
Undecane	13.833	11.199	9.207	7.662	6.54	5.59	4.929
Naphthalene	21.913	17.759	14.562	12.06	10.17	8.624	7.485
Dodecane	27.976	21.921	17.44	14.015	11.562	9.535	8.117
(C) Mixture 3							
T/K		343.7	348.8	353.85	359	364	369.05
Methane[a]		1.319	1.317	1.329	1.341	1.351	1.35
n-Heptane		1.805	1.735	1.688	1.653	1.623	1.59
Methylcyclohexane		1.961	1.872	1.809	1.76	1.718	1.675
1-Octene		2.398	2.234	2.101	1.998	1.915	1.844
Nonane		3.863	3.421	3.078	2.805	2.587	2.406
Cubane		5.481	4.78	4.219	3.772	3.413	3.12
exo-THDCPD[b]		10.491	8.994	7.494	6.423	5.594	5.012
endo-THDCPD[b]		12.463	10.508	8.751	7.447	6.43	5.678
(D) Mixture 4							
T/K	343.6	348.8	353.85	359.0	364	369.1	374.2
Methane[a]	1.295	1.301	1.295	1.304	1.315	1.326	1.325
n-Heptane	1.854	1.78	1.720	1.674	1.636	1.608	1.575
Methylcyclohexane	2.018	1.924	1.845	1.784	1.734	1.693	1.652
1-Octene	2.464	2.286	2.142	2.028	1.934	1.855	1.79
Nonane	3.952	3.495	3.128	2.84	2.609	2.421	2.263
Cubane	5.59	4.862	4.340	3.815	3.507	3.159	2.872
exo-THDCPD[b]	10.689	8.95	7.582	6.504	5.632	4.882	4.378
endo-THDCPD[b]	12.715	10.654	8.868	7.54	6.478	5.593	4.946

[a] Non-retained reference.

[b] Tetrahydrodicyclopentadiene.

run isothermally using either a 15 or 30 m SPB-5 capillary column. Helium was used as the carrier gas. At the temperatures of the experiments, the retention time of the solvent, CH_2Cl_2, decreased with increasing temperature suggesting that it was retained by the column. Methane was bubbled prior to each run and its retention time was found to increase with temperature. A consequence of the increase in viscosity of the carrier gas with temperature, this is the criterion used to confirm that a substance is not retained on the column and can be used to determine the dead volume of the column. The gas chromatographic retention times of cubane and the standards are summarized in Table 1. Adjusted retention times, t_a, were calculated by subtracting the measured retention time of methane from the retention time of each analyte as a function of temperature usually over a 30 K range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke 51 K/J thermometer. Temperature was maintained constant by the gas chromatograph to ±0.1 K.

3. Results

Cubane was analyzed using a series of different standards in four separate mixtures. The literature values of the standards are reported in Table 2. Standards were chosen on the basis of their relative retention times, our assessment of the reliability of their vaporization enthalpies and their structural similarities to cubane. A plot of $\ln(1/t_a)$ against $1/T$(K) resulted in straight lines characterized by the parameters listed in the second and third columns of Table 3. Equations for the correlation of enthalpies of transfer from solution to the vapor, $\Delta_{\mathrm{sln}}{}^{v}H_{\mathrm{m}}(T_{\mathrm{m}})$, against experimental vaporization enthalpies are given at the bottom of Table 3 for each correlation. A graphical summary of how well experimental vaporization enthalpies were reproduced is given in Fig. 1. The equation describing the correlation between experimental and calculated values of $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) is provided in the caption of Fig. 1. The mean vaporization enthalpy of cubane at $T = 298.15$ K ((44.6 ± 1.6) kJ mol^{-1}) and of the reference materials resulting from the four correlations are summarized in Table 4.

Table 2
Literature values used as reference for cubane; molar enthalpies in kJ mol^{-1}

	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$(298.15 K)	Reference
Norbornene	35.1 ± 0.2	[9]
Methylcyclohexane	35.4	[10]
Heptane	36.57 ± 0.18	[11]
1-Octene	40.3 ± 0.2	[12]
Octane	41.56 ± 0.2	[11]
Nonane	46.55 ± 0.46	[11]
Adamantane	48.2	[13]
exo-Tetrahydrodicyclopentadiene	49.1 ± 2.3	[14]
endo-Otetrahydrodicyclopentadiene	50.2 ± 2.3	[14]
Decane	51.42 ± 0.26	[11]
Naphthalene	55.65 ± 2.8	[15]
Undecane	56.58 ± 0.56	[11]
Dodecane	61.52 ± 0.61	[11]

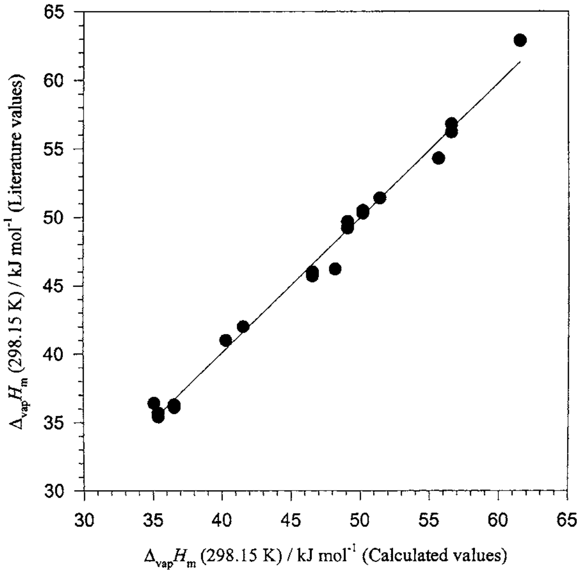

Fig. 1. The correlation between experimental and calculated vaporization enthalpies of the standards used in four separate correlations. The equation of the line calculated by a linear regression analysis is given by: $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (kJ mol^{-1}) (lit) = (1.004 ± 0.034$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (calcd) − (0.15 ± 0.98).

Solid phase transitions of cubane have been previously measured by adiabatic calorimetry and DSC [17]. Two phase transitions have been observed in the solid state of cubane, a solid–solid transition at $T_{\mathrm{tr}} = (394.02 \pm 0.04)$ K ($\Delta_{\mathrm{tr}}H_{\mathrm{m}}$(5.94 ± 0.02) kJ mol^{-1}) measured by adiabatic calorimetry and T_{fus}(onset) = (404.9 ± 0.5) K ($\Delta_{\mathrm{fus}}H_{\mathrm{m}}$(8.7 ± 0.3) kJ mol^{-1}) measured by DSC [17]. Since both of these transitions occur above $T = 298.15$ K, both must be taken into account in calculating the sublimation enthalpy of cubane at $T = 298.15$ using the following thermodynamic equality:

$$\Delta_{\mathrm{sub}}H_{\mathrm{m}}(298.15\,\mathrm{K}) = \Delta_{\mathrm{vap}}H_{\mathrm{m}}(298.15\,\mathrm{K}) + \Delta_{\mathrm{cr(2)}}{}^{1}H_{\mathrm{m}}(298.15\,\mathrm{K}) \qquad (1)$$

where $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) represents the vaporization enthalpy at $T = 298.15$ K and $\Delta_{\mathrm{cr(2)}}{}^{1}H_{\mathrm{m}}$(298.15 K) represents the sum of the measured phase transition and fusion enthalpy adjusted to $T = 298.15$ K.

The vaporization enthalpy of cubane at $T = 298.15$ K is obtained directly by correlation gas chromatography. Adjustment of the total phase change enthalpy from $T = T_{\mathrm{fus}}$ to $T = 298.15$ K is necessary because of the difference in heat capacity of the crystalline and liquid phases. A protocol for doing this is described below (Eqs. (4) and (5)); the method has recently been tested [18]. Inclusion of the temperature adjustment, which is small, results in a sublimation enthalpy for cubane at $T = 298.15$ K of (55.2 ± 2.0) kJ mol^{-1}. These results are summarized in Table 5. This value is considerably

Table 3

	$\Delta_{\mathrm{sln}}{}^{v}H_{\mathrm{m}}(T_{\mathrm{m}})/R$	Intercept	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) (lit)	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ (298.15 K) (calc)
(A) Mixture 1[a]				
$T_{\mathrm{m}} = 361\,\mathrm{K}$				
Cubane	4086.2	10.477		45.6
Nonane	4130.5	11.102	46.55	46.0
exo-THDCPD[b]	4533.4	11.028	49.1	49.7
endo-THDCPD[b]	4617.7	11.054	50.2	50.5
Decane	4713.1	11.996	51.42	51.4
Undecane	5232.7	12.733	56.58	56.2
(B) Mixture 2[c]				
$T_{\mathrm{m}} = 359\,\mathrm{K}$				
Norbornene	3772.8	11.351	35.1	36.4
Octane	4214.6	12.077	41.56	42.0
Cubane	4332.1	11.176		43.6
Adamantane	4539.4	10.909	48.2	46.2
Naphthalene	5163.4	12.008	55.65	54.3
Undecane	5358.1	13.074	56.58	56.8
Dodecane	5835.5	13.71	61.52	62.9
(C) Mixture 3[d]				
$T_{\mathrm{m}} = 356\,\mathrm{K}$				
Methylcyclohexane	3417.9	10.389	35.40	35.1
n-Heptane	3544.4	11.036	36.57	36.5
1-Octene	3951.2	11.421	40.3	41.0
Cubane	4292.3	11.065		44.7
Nonane	4411.4	11.904	46.55	46.1
exo-THDCPD[b]	4693.2	11.436	49.10	49.1
endo-THDCPD[b]	4793.4	11.535	50.20	50.2
(D) Mixture 4[e]				
$T_{\mathrm{m}} = 356\,\mathrm{K}$				
Methylcyclohexane	3346.6	10.063	35.40	35.7
n-Heptane	3385.7	10.434	36.57	36.1
1-Octene	3898.0	11.19	40.3	41.0
Cubane	4256.3	10.927		44.4
Nonane	4386.0	11.789	46.55	45.7
exo-THDCPD[b]	4763.0	11.622	49.10	49.3
endo-THDCPD[b]	4870.3	11.736	50.20	50.3

[a] ΔH_{vap} (298.15 K)/kJ mol^{-1} = (1.117 ± 0.085) $\Delta_{\mathrm{sln}}{}^{v}H_{\mathrm{m}}(361\,\mathrm{K})$ + (7.63 ± 0.56); $r^2 = 0.9829$.

[b] Tetrahydrodicyclopentadiene.

[c] $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K)/kJ mol^{-1} = (1.55 ± 0.11) $\Delta_{\mathrm{sln}}{}^{v}H_{\mathrm{m}}(359\,\mathrm{K})$ − (12.24 ± 1.55); $r^2 = 0.9809$.

[d] $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ mol^{-1} = (1.321 ± 0.041) $\Delta_{\mathrm{sln}}{}^{v}H_{\mathrm{m}}(\mathbf{356}\,\mathrm{K})$ − (2.39 ± 0.45); $r^2 = 0.9961$.

[e] $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ mol^{-1} = (1.157 ± 0.052) $\Delta_{\mathrm{sln}}H_{\mathrm{m}}(359\,\mathrm{K})$ + (3.52 ± 0.64); $r^2 = 0.9921$.

smaller than the value of (80.3 ± 1.7) kJ mol^{-1} measured by Knudsen effusion reported previously [4].

4. Discussion

The sublimation enthalpy of cubane has previously been calculated by the atom–atom potential method. The value calculated, 62.8 kJ mol^{-1} [19], is in reasonably good agreement with the value of (55.2 ± 2.0) kJ mol^{-1} obtained in this study. V.V. Diky et al. in their article questioning the sublimation enthalpy of cubane demonstrate that the sublimation enthalpies of a variety of saturated cyclic and polycyclic hydrocarbons correlate on a qualitative basis, with their molar mass. A graph similar to theirs is reproduced in Fig. 2 using the data in Table 6 obtained from recent compendia [20–22] and includes the sublimation enthalpy of cubane determined previously (●) and by this work (■). Literature vaporization and sublimation enthalpies, columns 2 and 3 of Table 6, were adjusted to $T = 298.15\,\mathrm{K}$ when necessary, using Eqs. (2) and (3), respectively. The sublimation enthalpy of the rigid solid, [$\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (298.15 K)] column 10, Table 6, was calculated by combining the sublimation enthalpy with all solid–solid phase transitions occurring between $T = 0\,\mathrm{K}$, and the temperature(s) at which the sublimation enthalpy was measured, columns 3 and 4. For compounds that are liquids at $T = 298.15\,\mathrm{K}$, the vaporization enthalpy was adjusted to $T = 298.15\,\mathrm{K}$ using Eq. (2) when necessary and the

Table 4
Summary of vaporization enthalpies; by correlation and from the literature

	$\Delta_{vap}H_m$ (298.15 K) (lit)	Mix 1	Mix 2	Mix 3	Mix 4	$\Delta_{vap}H_m$ (298.15 K) mean
Norbornene	35.1		36.4			36.4
Methylcyclohexane	35.4			35.1	35.7	35.4
Heptane	36.57			36.5	36.1	36.3
1-Octene	40.3			41.0	41.0	41.0
Octane	41.56		42.0			42.0
Cubane		45.6	43.6	44.7	44.4	44.6 ± 1.6[b]
Nonane	46.55	46.0		46.1	45.7	45.9
Adamantane	48.2		46.2			46.2
exo-THDCPD[a]	49.1	49.7		49.1	49.3	49.2
endo-THDCPD[a]	50.2	50.5		50.2	50.3	50.3
Decane	51.42	51.4				51.4
Naphthalene	55.65		54.3			54.3
Undecane	56.58	56.2	56.8			56.5
Dodecane	61.52		62.9			62.9

[a] Tetrahydrodicyclopentadiene.
[b] (±2) standard deviations.

fusion enthalpy was adjusted to $T = 298.15$ K using Eq. (4) [16,18]. Their sum (columns 2 and 9), combined with any solid–solid phase transitions observed (column 4), are also listed in column 10. Sublimation enthalpies of the rigid solid were calculated in a slightly different manner by Diky et al. [7]; however, the results compare favorably. All heat capacities, in column 6 were estimated unless noted otherwise.

$$\Delta_{vap}H_m(298.15\,\mathrm{K})\ (\mathrm{kJ\,mol^{-1}}) = \Delta_{vap}H_m(T_m) + \frac{(10.58 + 0.26\mathrm{Cp_l})(T_m - 298.15)}{1000} \tag{2}$$

$$\Delta_{sub}H_m(298.15\,\mathrm{K})\ (\mathrm{kJ\,mol^{-1}}) = \Delta_{sub}H_m(T_m) + \frac{(0.75 + 0.15\mathrm{Cp_{cr}})(T_m - 298.15)}{1000} \tag{3}$$

$$\Delta_{fus}H_m(298.15\,\mathrm{K})/\mathrm{kJ\,mol^{-1}} = \Delta_{fus}H_m(T_{fus}) + \Delta_{cr}{}^{1}\mathrm{Cp_m}\Delta T, \tag{4}$$

Table 5
Phase change enthalpies of cubane; enthalpies in $\mathrm{kJ\,mol^{-1}}$

$\Delta_{cr(2)}{}^{cr(1)}H_m(394\,\mathrm{K})$ (lit)[a]	5.94 ± 0.02
$\Delta_{cr(1)}{}^{cr(1)}H_m(T_{fus})$ (lit)[a]	8.7 ± 0.3
T_{fus} (K)	404.9
$\Delta_{cr}{}^{1}Cp_m\Delta T\,\mathrm{kJ\,mol^{-1}}$[b]	−4.02 ± 1.2
$\Delta_{cr(2)}{}^{1}H_m(298\,\mathrm{K})$	10.6 ± 1.2
$\Delta_{vap}H_m$ (298 K)[c]	44.6 ± 1.6
$\Delta_{sub}H_m$ (298 K)	55.2 ± 2.0

[a] [17].
[b] The experimental heat capacity of the crystal at $T = 298.15$ K was obtained graphically [17]: Cp(cr) = 125 J mol^{-1} K^{-1}; the heat capacity of the liquid phase of cubane was estimated [16]: CpQ(l) = 179.2 J mol^{-1} K^{-1}; the total phase change enthalpy, $\Delta_{cr(2)}{}^{1}H_m(T_{fus})$ was adjusted to $T = 298.15$ K using Eq. (4) [18]; the uncertainty (±2σ) assumed to be 0.3 of the magnitude of the temperature adjustment, see [18] for further details.
[c] Uncertainty in vaporization enthalpy represents ±2σ.

where

$$\Delta_{cr}{}^{1}\mathrm{Cp_m}\Delta T\ (\mathrm{kJ\,mol^{-1}}) = [0.15\mathrm{Cp(cr)} - 0.26\mathrm{Cp(1)} - 9.83]\left(\frac{T_{fus} - 298.15}{1000}\right). \tag{5}$$

A treatment of the data in the graph by a linear regression analysis, excluding cubane from the analysis, results in the following relationship between sublimation enthalpy and molar mass (*M*):

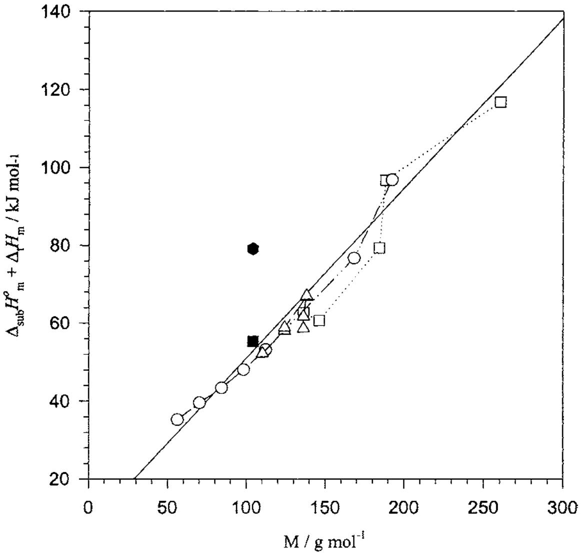

Fig. 2. Relation of enthalpies of sublimation of the rigid solid ([$\Delta_{sub}H_m$]) at $T = 298.15$ K to their molar masses, *M* adapted from reference [7]. Cage hydrocarbons (□); bicyclic compounds (△); cyclic compounds (○). Cubane: (■) this work. Cubane: (⬢) lit. [4]. The solid line was obtained by a linear regression analysis.

Table 6
Enthalpies of sublimation of saturated cyclic hydrocarbons and auxiliary data[a]

	$\Delta_{\text{vap}}H_{\text{m}}$ (298 K)	$\Delta_{\text{sub}}H_{\text{m}}$ (298 K)	$\Delta_{\text{tr}}H_{\text{m}}$ (T_{tr})	T_{tr} (K)	Cp(l)/Cp(cr)	$\Delta_{\text{fus}}H_{\text{m}}$ (T_{fus})	T_{fus} (K)	$\Delta_{\text{fus}}H_{\text{m}}$ (298 K)	$[\Delta_{\text{sub}}H_{\text{m}}]$[b] (298 K)	M (g/mol)	$\Delta_{\text{sub}}H_{\text{m}}$ (298 K) Calc.
Cyclic compounds											
Cyclobutane	24.1		5.71	145.7	104/98.4	1.09	182.4	5.4	35.3	56.11	30.5
Cyclopentane	28.5		4.9	122	130/123						
			0.34	138		0.6	179.7	5.84	39.6	70.1	36.4
Cyclohexane	33.04		6.74	186.1	155/148	2.68	279.8	3.62	43.4	84.16	42.4
Cycloheptane	38.53		4.97	134.8							
			0.29	198.2							
			0.45	212.4	181/172	1.89	265.1	3.8	48.0	98.19	48.4
Cyclooctane	43.35		6.31	166.5	207/197						
			0.48	183.8		2.41	287.9	3.1	53.25	112.21	54.3
Cyclododecane		76.1	0.6	199					76.7	168.32	78.2
Cyclotetradecane		96.8							96.8	192.3	88.4
Bicyclic and tricyclic compounds											
Bicyclo[2.2.2]octane		47.7	4.6	164.3			52.3	110.2	53.5		
cis-PHI[c]	46.12		8.26	182.3							
			0.39	184.5	223/196	1.4	236.5	3.3	58.1	124.2	59.4
trans-PHI[c]	44.76				223/196	10.9	213.9	14.1	58.9	124.2	59.4
cis-Decalin	50.1		2.14	216.1	248/220	9.49	230.2	14.6	66.8	138.3	65.4
trans-Decalin	48.5				248/220	14.4	242.8	18.6	67.1	138.3	65.4
endo-HDCPD[d]		51	10.7	213.8					61.7	136.2	64.5
exo-THDCPD[d]	49.1		3.18	162.1	238/194	1.2	183.2	6.35	58.6	136.2	64.5
Cage compounds											
Cubane									55.2	104.2	50.9
Adamantane		59.3[e]	3.38	208.7					62.6	136.2	64.5
PCU[f]		55.85	4.86						60.7	146.2	68.8
HCTD[g]		79.29							79.3	184.3	84.9
Diamantane		96.77							96.77	188.3	86.7
Pagodane[h]		116.8			/263				116.8	260.4	117.3

[a] Enthalpies in kJ mol^{-1}; estimated heat capacities of the liquid/crystal (Cp(l)/Cp(cr) in J mol^{-1} K^{-1} [16]; phase change enthalpies were obtained from references [20–22] unless referenced otherwise.

[b] $[\Delta_{\text{sub}}H_{\text{m}}](298) = \Delta_{\text{vap}}H_{\text{m}}$ (298) + $\Delta_{\text{fus}}H_{\text{m}}$ (298) + $\Sigma\Delta_{\text{trr}}H_{\text{m}}$ (T_{tr}) or $\Delta_{\text{sub}}H_{\text{m}}$ (298) + $\Sigma\Delta_{\text{tr}}H_{\text{m}}$ (T_{tr}); sublimation of the rigid crystal.

[c] Perhydroindane [7].

[d] Tetrahydrodicyclopentadiene [14].

[e] Average of six values reported at T = 298.16 K [20].

[f] Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane [26].

[g] Heptacyclo[6.6.0^{2},^{6}.0^{3},^{13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane [28].

[h] Adjusted to T = 298.15 K using Eq. (3) using an estimated Cp(cr) of 263 J mol^{-1} K^{-1} [29].

$$\Delta_{\text{sub}}H_{\text{m}}(298.15\,\text{K})\ (\text{kJ mol}^{-1}) = (0.425 \pm 0.023)M + (6.64 \pm 4.6); \qquad r^2 = 0.9535 \tag{6}$$

The sublimation enthalpy of cubane calculates to (50.9 ± 4.6) kJ mol^{-1} according to this equation. The results calculated using this equation are included as the last column in Table 6. The experimental sublimation enthalpy of cubane is within the uncertainty of the correlation.

Using the group contribution method reported by Diky et al. [7] for estimating the sublimation enthalpy of the rigid crystalline state, a group value of (5.52 ± 0.41) kJ mol^{-1} is derived for a cyclic tertiary sp^3 carbon from bicyclic and polycyclic model compounds containing five and six membered rings. This computes to a sublimation enthalpy of (44.2 ± 3.3) kJ mol^{-1} estimated for cubane. The experimental value determined is about 10 kJ mol^{-1} larger. Using the values reported in Table 6 to generate group values for cyclic tertiary and secondary sp^3 hybridized carbon atoms result in near identical group values, 5.59 and 6.87 kJ mol^{-1}, respectively.

The sublimation enthalpy of cubane can also be estimated by combining an estimated vaporization enthalpy with the experimental fusion enthalpy. Using the following equation for predicting the vaporization enthalpy of a hydrocarbon [23]:

$$\Delta_{\text{vap}}H_{\text{m}}(298.15\,\text{K})\ (\text{kJ mol}^{-1}) = 4.69(n_{\text{C}} - n_{\text{Q}}) + 1.3n_{\text{Q}} + 3.0 \tag{7}$$

where n_{C} equals the number of carbon atoms and n_{Q} refers to the number of quaternary carbons, a vaporization enthalpy of 40.5 kJ mol^{-1} results. Addition of the temperature adjusted fusion enthalpy of 10.6 kJ mol^{-1} result in an estimated sublimation enthalpy of 51.1 kJ mol^{-1}, a value in good agreement with the experimental determination of (55.2 ± 2.0) $\mathrm{kJ\,mol^{-1}}$.

As noted by Diky et al. [7], the sublimation enthalpy of cyclotetradecane, also measured by Knudsen effusion by the same laboratory reporting the cubane results [24], is similarly much larger than results reported by others for the same compound [25–27].

The enthalpy of formation of crystalline cubane [4], is also subject to question. The value of $541.8\,\mathrm{kJ\,mol^{-1}}$ derived from combustion measurements ($\Delta_c E^\circ = -4828.3$ $\mathrm{kJ\,mol^{-1}}$), was corrected for an unspecified amount of ill-defined carbon adhering to the walls of the bomb. Unraveling of this portion of the problem will also require additional experimental measurements.

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