JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

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The Joining of Measurement and Prediction: The Enthalpy of Formation of 1,4-Cubanedicarboxylic Acid

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Supporting Information

ABSTRACT: This study is a multidisciplinary contribution to the thermochemistry of 1,4-cubanedicarboxylic acid (pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1,4-dicarboxylic acid). An isoperibolic static microbomb calorimeter was used to determine the enthalpy of formation in the condensed phase at $T = 298.15$ K as $\Delta_f H_m^\circ(\mathrm{cr}) = (-355.9 \pm 11.7)\ \mathrm{kJ \cdot mol^{-1}}$. The enthalpy of sublimation was obtained by combining the vaporization enthalpy evaluated by correlation-gas chromatography and the fusion enthalpy measured by differential scanning calorimetry and adjusted to $T = 298.15$ K, which afforded the value $\Delta_{\mathrm{sub}} H_m(298.15\ \mathrm{K}) = (126.5 \pm 9.0)\ \mathrm{kJ \cdot mol^{-1}}$. Combination of these two enthalpies gave $\Delta_f H_m^\circ(\mathrm{g}, 298.15\ \mathrm{K}) = (-229.4 \pm 14.8)\ \mathrm{kJ \cdot mol^{-1}}$. Additionally the enthalpy of sublimation of 1-adamantanecarboxylic acid (tricyclo[3.3.1.1^{3,7}]decane-1-carboxylic acid) was determined as $\Delta_{\mathrm{sub}} H_m(298.15\ \mathrm{K}) = (98.7 \pm 4.5)\ \mathrm{kJ \cdot mol^{-1}}$. By means of theoretical calculations using isodesmic reactions, the enthalpy of formation of 2,6-cuneanedicarboxylic acid (pentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octane-2,6-dicarboxylic acid) was calculated. Strain energies of cubane and cuneane dicarboxylic acids were also calculated.

INTRODUCTION

Cubane (pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane) and its derivatives are saturated polycycloalkanes in which there has been considerable interest[1,2] because of their high strain energy, multiple substitution possibilities, symmetry, and structural aesthetics alike. Soon after the first successful synthesis of the parent hydrocarbon in 1964,[3] the enthalpies of formation of the parent hydrocarbon in the solid and gas phases were determined using combustion calorimetry and mass effusion.[4] Recently, however, considerable doubt has been raised—and eventually resolved—regarding the sublimation enthalpy that interrelates these two phases.[5−8] Unlike adamantane (tricyclo[3.3.1.1^{3,7}]decane), another highly symmetric and aesthetic saturated polycycloalkane for which the enthalpy of formation of many derivatives has been measured,[9−11] there are but four cubane derivatives for which such data are directly available from combustion calorimetry experiments, namely, the 1,4-dicarboxylic acid[12] and its dimethyl,[5,12,13] diisopropyl,[12] and bis(2-fluoro-2,2-nitroethyl) esters.[12] Through the use of judicious gas-phase hydrogen atom and proton transfer reactions interrelating cubene radical anion and the neutral hydrocarbon, cubyl radical and cubene radical anion, and cubane and cubyl radical, the dehydrogenation enthalpy of cubane to form cubene has been determined.[14] For several iodinated cubane derivatives, temperatures, phase-change enthalpies, and entropies of transition have also been measured.[15] The value for the dimethyl ester has also been a source of contention;[5,12,13,16] this is the only cubane derivative for which the value for the gas-phase species has been determined.[13] We reenter the fray by presenting here the results of our measurements and accompanying theoretical analysis for 1,4-cubanedicarboxylic acid in both the solid and gas phases. The sublimation enthalpy of 1-adamantanecarboxylic acid was also determined, providing a missing value necessary for the isodesmic reactions described below. From theoretical calculations, the enthalpy of formation of the unknown isomer 2,6-cuneanedicarboxylic acid was also obtained. The structures of 1,4-cubanedicarboxylic acid (pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1,4-dicarboxylic acid) and 2,6-cuneanedicarboxylic acid (pentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octane-2,6-dicarboxylic acid) are provided in Figure 1.

EXPERIMENTAL SECTION

Materials. Purified cubanedicarboxylic acid was kindly supplied to us by Dr. A. Bashir-Hashemi (ERC at AFRL/PRSP), to whom we are very grateful. The material for the combustion experiments was used as provided, and that used for the differential scanning calorimetry (DSC) experiments was additionally recrystallized from glacial acetic acid and dried.[17] 1-Adamantanecarboxylic acid (0.99 mass fraction) and all the other alkanoic acids used in this study were purchased from Aldrich

Special Issue: John M. Prausnitz Festschrift

Received: October 28, 2010
Accepted: December 31, 2010
Published: February 07, 2011

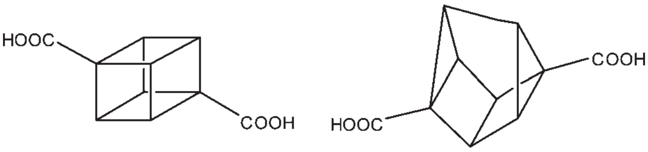


Figure 1. Structures of 1,4-cubanedicarboxylic acid and 2,6-cuneanedicarboxylic acid.

Table 1. Physical Properties at T = 298.15 K

	M	ρ	$10^{-7}\cdot(\delta V/\delta T)_p$	c_p
compound	$g\cdot mol^{-1}$	$g\cdot cm^{-3}$	$dm^3\cdot g^{-1}\cdot K^{-1}$	$J\cdot K^{-1}\cdot g^{-1}$
benzoic acid	122.1213	1.32	3.85	1.21
Vaseline	14.0266	0.870[a]	8.374[b]	2.22[b]
cotton	27.700	1.5[c]	9.69[c]	1.48
1,4-cubanedicarboxylic acid	192.17	1.64[d]	3.35	0.95

[a] Value taken from ref 21. [b] Value taken from ref 22. [c] Value taken from ref 23. [d] Value taken from ref 12.

Table 2. Measurement of the Total Solid−Liquid Phase-Change Enthalpies of 1,4-Cubanedicarboxylic Acid and 1-Adamantanecarboxylic Acid

mass	$\Delta H_{\mathrm{tpce}}(T_{\mathrm{ot}})$[a]	T_{ot}	$\Delta H_{\mathrm{tpce}}(T_{\mathrm{ot}})_{\mathrm{avg}}$	$T_{\mathrm{ot,avg}}$
mg	$kJ\cdot mol^{-1}$	K	$kJ\cdot mol^{-1}$	K
		1,4-Cubanedicarboxylic Acid		
5.16	18.0	495.4	17.4 ± 1.2	495.0
3.56	15.6	493.5		
3.83	18.8	495.2		
5.18	17.5	495.3		
3.23	17.2	495.5		
		1-Adamantanecarboxylic Acid		
16.01	16.12	447.6	16.2 ± 0.4	447.2
10.06	15.93	447.1		
10.89	16.8	447.1		
10.27	16.0	447.1		

[a] T_{ot} = onset temperature; $\Delta H_{\mathrm{tpce}}(T_{\mathrm{ot}})$ for 1-adamantanecarboxylic acid refers to the fusion enthalpy.

and used as received. All were analyzed by gas chromatography and found to have mass-fraction purities of 0.97 or better.

Combustion Experiments. The energy of combustion of 1,4-cubanedicarboxylic acid was determined in an isoperibolic static microbomb calorimeter developed in Madrid.[18,19] The calorimetric temperatures were measured to within $\pm 1\cdot 10^{-4}$ K by means of a 100 Ω platinum resistance thermometer using a calibrated resistance bridge (model F300, Automatic System Laboratories Ltd.) interfaced to a microcomputer programmed to calculate the adiabatic temperature change. The energy of reaction was always referenced to the final temperature of T = 298.15 K. Because of the high reactivity and exothermicity associated with the combustion of 1,4-cubanedicarboxylic acid, in order to obtain CO_2 as the sole carbon-containing product, several methods and auxiliary substances were examined. The best results were obtained at an oxygen pressure of 2.03 MPa using benzoic acid (NIST standard reference sample 39j) and Vaseline as combustion aids. A pellet of benzoic acid was placed in the bottom of the crucible below the 1,4-cubanedicarboxylic acid pellet, both of which were first coated with Vaseline. The two pellets and the auxiliary substance were weighed in the platinum crucible. To verify complete combustion at the end of each experiment, the total quantity of gas in the bomb was slowly released ($0.2\ cm^3\cdot s^{-1}$) through Dräger tubes. No traces of CO were detected (sensitivity levels were approximately $1\cdot 10^{-6}$ mass fraction). In addition, no traces of carbon residue were observed in any of the runs reported in Table 2. Experiments in which carbon (as soot traces) was observed were rejected. The massic energy of combustion of the compound was determined by burning the samples in oxygen with 0.05 cm^3 of water added to the bomb. The combustion bomb was flushed and filled with oxygen, previously freed from combustible impurities, at an initial pressure of 2.03 MPa. The energy equivalent of the calorimeter, ε(calor), was determined from the combustion of NIST 39j benzoic acid at a pressure of 2.03 MPa. From 10 calibration experiments, ε(calor) was determined to be (2108.42 ± 0.48) $J\cdot K^{-1}$, where the uncertainty quoted is the standard deviation of the mean. The empirical formula and massic energy of combustion of the cotton-thread fuse used in the experiments with this microbomb [$C_{1.000}H_{1.740}O_{0.871}$ and (−17410 ± 37) $J\cdot g^{-1}$, respectively] were determined in our laboratory. The massic energy of combustion of Vaseline used was (−46086 ± 5) $J\cdot g^{-1}$.[20] All of the samples were weighed on a Mettler UMX2 ultramicrobalance, and corrections of apparent mass to mass were made. For corrections of apparent mass to mass, conversion of the energy of the actual bomb process to that of the isothermal process, and corrections to the standard state, the values of density (ρ), massic heat capacity (c_p), and $(\delta V/\delta T)_p$ provided in Table 1 were used. An estimated pressure coefficient of specific energy, $(\delta u/\delta p)_T$, of $-0.2\ J\cdot g^{-1}\cdot MPa^{-1}$ at T = 298.15 K (a typical value for most solid organic compounds) was assumed for 1,4-cubanedicarboxylic acid. Its heat capacity was determined in this work using DSC. Standard-state corrections were made according to Hubbard et al.[24] The atomic weights of the elements used were those recommended by IUPAC in 2005.[25]

DSC Experiments. DSC measurements for both 1,4-cubanedicarboxylic acid and 1-admantanecarboxylic acid were performed on a PerkinElmer DSC 7 instrument calibrated using indium as a standard. In view of the fact that 1,4-cubanedicarboxylic acid decomposes upon melting, a total of five runs were performed to evaluate the reproducibility of the results. The results for both acids are summarized in Table 2, and those for 1,4-cubanedicarboxylic acid are discussed below.

Vaporization Enthalpy. The vaporization enthalpy of 1,4-cubanedicarboxylic acid and 1-adamantanecarboxylic acid were evaluated by correlation-gas chromatography. Details regarding the applicability of this technique for the evaluation of carboxylic acids have previously been reported.[26,27] Since both species were analyzed as mixtures that were separated by the chromatography, the initial purity of these materials was not as critical as in studies where the thermochemical properties are highly dependent on purity. Correlation gas chromatography experiments were performed on an HP 5890 gas chromatograph equipped with a flame ionization detector and run at a split ratio of approximately 100/1. Retention times were recorded on an HP 3356 Series II integrator. The compounds were run isothermally on a 30 m SP-5 column. While enthalpies of transfer do depend on the nature of the column used, the results following the correlation

Table 3. Adjustment of the Vaporization Enthalpies of the Alkanoic Acids to T = 298.15 K

	lit $\Delta_{\text{vap}}H^{\circ}_{\text{m}}(T_{\text{m}})$	T_{m}	$C_{p,\text{l}}$ [c]	$\Delta_{\text{vap}}H^{\circ}_{\text{m}}$(298 K)/kJ·mol^{-1}	
acid	kJ·mol^{-1}	K	J·mol^{-1}·K^{-1}	lit	avg
decanoic acid	88.6 [a]	314	377.5	90.3	90.3
undecanoic acid	81.3 [b]	408	409.4	94.16	93.88
	90.7 [a]	323	409.4	93.61	
dodecanoic acid	88.8 [b]	408	441.3	102.57	100.81
	96.7 [a]	317	441.3	99.06	
tridecanoic acid	90.1 [b]	424	473.2	106.92	106.45
	100.4 [a]	340	473.2	106.0	
tetradecanoic acid	91.6 [b]	438	505.1	111.45	111.38
	104.1 [a]	349	505.1	111.32	
pentadecanoic acid	94.7 [b]	446	537.0	116.21	116.77
	108.5 [a]	357	537.0	117.34	

[a] Value taken from ref 28. [b] Value taken from ref 29. [c] Data taken from ref 30.

Table 4. Results of the Combustion Experiments on 1,4-Cubanedicarboxylic Acid at T = 298.15 K[a]

m(compound)/mg[b]	10.1992	10.7064	10.3668	10.1192	9.6993	10.3361	10.1902
m'(benzoic acid)/mg[b]	35.0813	34.7031	34.9364	46.4386	46.7653	45.7750	46.2311
m''(Vaseline)/mg[b]	16.3319	8.3688	13.4216	16.1030	15.1169	17.6369	15.5944
m'''(fuse)/mg[b]	0.5725	0.4820	0.5020	0.5619	0.3953	0.4394	0.5726
ΔT_{c}/K[c]	0.9209	0.7465	0.8570	1.0575	1.0327	1.0831	1.0444
ε(calor)($-\Delta T_{\text{c}}$)/J [d]	−1941.57	−1573.71	−1806.69	−2229.35	−2176.98	−2283.36	−2201.94
ε(cont.)($-\Delta T_{\text{c}}$)/J [e]	−0.69	−0.52	−0.62	−0.80	−0.73	−0.83	−0.79
ΔU_{ign}/J [f]	0.43	0.43	0.43	0.43	0.43	0.43	0.43
ΔU_{dec}(HNO_3)/J [g]	0.47	0.24	0.24	0.24	0.29	0.24	0.24
ΔU(corr. to std states)/J [h]	0.86	0.74	0.81	1.06	1.04	1.07	1.05
$-m'\Delta_{\text{c}}u°$(benzoic acid)/J	926.64	916.65	922.81	1226.63	1235.26	1209.10	1221.15
$-m''\Delta_{\text{c}}u°$(Vaseline)/J	752.69	385.69	618.56	742.14	696.69	812.83	718.70
$-m'''\Delta_{\text{c}}u°$(fuse)/J	9.98	8.40	8.75	9.80	6.89	7.66	9.98
$\Delta_{\text{c}}u°$(compound)/kJ·g^{-1}	−24.6288	−24.47876	−24.66623	−24.69047	−24.44603	−24.46384	−24.64925
$\langle\Delta_{\text{c}}u°$(298.15 K)$\rangle$/kJ·g^{-1}				−24.5748 ± 0.0293			

[a] For definitions of the symbols, see refs 24 and 35. T_{th} = 298.15 K; V_{bomb} = 0.022 dm^3; $p^{\text{i}}_{\text{gas}}$ = 2.03 MPa; $m^{\text{i}}_{\text{water}}$ = 0.05 g. [b] Masses were obtained from the apparent masses. [c] $\Delta T_{\text{c}} = T_{\text{f}} - T_{\text{i}} + \Delta T_{\text{corr}}$. [d] ε(calor) = energy equivalent of the whole system less the contents of the bomb. [e] ε(cont.) = energy equivalent of the contents of the bomb; $\varepsilon(\text{cont.})(-\Delta T_{\text{c}}) = \varepsilon^{\text{i}}(\text{cont.})(T^{\text{i}} - 298.15\text{ K}) + \varepsilon^{\text{i}}(\text{cont.})(298.15\text{ K} - T^{\text{f}} + \Delta T_{\text{corr}})$. [f] Experimental energy of ignition. [g] Experimental energy of formation of nitric acid. [h] ΔU(corr. to std states) is the sum of items 81−85, 87−90, 93, and 94 in ref 24.

remained independent of the nature of the column within the reproducibility of the results. Helium was used as the carrier gas. Methanol, the solvent, was used as a nonretained reference. At the temperatures of these experiments, methanol was not retained by the column. Adjusted retention times, t_{a}, were calculated by subtracting the measured retention time of the nonretained reference from the retention time of each analyte as a function of temperature at 5 K intervals over a T range of 30 K. Column temperatures were controlled by the gas chromatograph and monitored independently using a Fluke digital thermometer. The temperature maintained by the gas chromatograph was constant to ± 0.1 K. Enthalpies of transfer were calculated as the product of the gas constant, R, and the slope of the line obtained by plotting $\ln(t_{\text{o}}/t_{\text{a}})$ versus $1/T$. All of the plots of $\ln(t_{\text{o}}/t_{\text{a}})$ versus $1/T$, where t_{o} = 1 min, were characterized by correlation coefficients $r^2 > 0.99$. The retention times measured for all analytes are reported in the Supporting Information. The uncertainties ($\pm\,\sigma$) reported in the last column in each section of Table 7 were calculated from the uncertainty in the slope and intercept of the equation listed at the bottom of that section. These uncertainties reflect the potential error in the absolute value of the vaporization enthalpy.

The vaporization enthalpies of all of the alkanedioic acids are available at T = 298.15 K.[26] The vaporization enthalpies of the alkanoic acids used as standards are available at the mean temperature of measurement.[27,28] Table 3 reports the literature values and their adjustment to T = 298.15 K. Equation 1 was used for the temperature adjustment:[30]

$$\Delta_{\text{vap}}H^{\circ}_{\text{m}}(298\text{ K}) = \Delta_{\text{vap}}H^{\circ}_{\text{m}}(T_{\text{m}}) + (10.58\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + 0.26C_{p,\,\text{l}})(T_{\text{m}} - 298.15\text{ K}) \qquad (1)$$

where $C_{p,\text{l}}$ is the heat capacity of the liquid, which was estimated by group additivity.[31]

Computational Details. Standard ab initio molecular orbital calculations[32] were performed with the Gaussian 03 series of programs.[33] For all of the species included in this study, full geometry optimizations were carried out at the HF/6-31G(d) level. The corresponding harmonic vibrational frequencies were evaluated at the same level of theory to confirm that the optimized structures found corresponded to minima of the potential energy surface and to evaluate the corresponding zero-point vibrational energies (ZPEs) and the thermal corrections at T = 298 K. The ZPEs were scaled by the empirical factor 0.9135.[34] All of the minima found at the HF/6-31G(d) level were again fully reoptimized at the MP2(FULL)/6-31G(d) level.

RESULTS AND DISCUSSION

The results of the combustion experiments are given in Table 4. The symbols in this table have the same meaning as those in ref 35, and the experimental values were derived similarly. The massic energy of combustion of the compound has been referenced to the final temperature of the experiments, T = 298.15 K. The uncertainties in the standard molar energy and enthalpy of combustion are twice the final overall standard deviation of the mean and were estimated as outlined by Olofsson.[36]

Table 5 gives the standard molar energy and enthalpy of combustion referenced to the following combustion reaction:

$$C_{10}H_8O_4(\text{cr}) + 10O_2(\text{g}) \rightarrow 10CO_2(\text{g}) + 4H_2O(\text{l}) \qquad (2)$$

The values of the standard molar enthalpies of formation of $H_2O(\text{l})$ and $CO_2(\text{g})$ at T = 298.15 K are (−285.830 ± 0.042 and −393.51 ± 0.13) kJ·mol^{-1}, respectively; these values were taken from CODATA.[37]

Table 5. Standard Molar Energy of Combustion and Enthalpies of Combustion and Formation for 1,4-Cubanedicarboxylic Acid at T = 298.15 K

$\Delta_c U_m^\circ$ kJ·mol^{-1}	$\Delta_c H_m^\circ$ kJ·mol^{-1}	$\Delta_f H_m^\circ(\text{cr})$ kJ·mol^{-1}
−4722.5 ± 11.6	−4722.5 ± 11.6	−355.9 ± 11.7

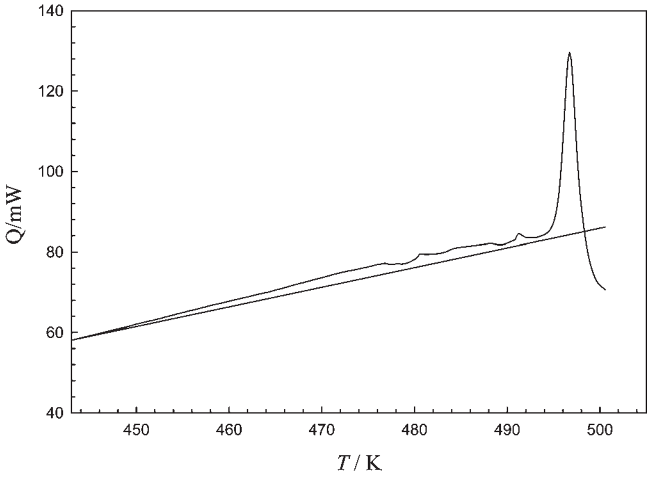


Figure 2. Typical DSC thermogram [heat flow (Q) as a function of temperature] for 1,4-cubanedicarboxylic acid obtained using a heating rate of 10 K·min^{-1}.

The condensed-phase enthalpy of formation of 1,4-cubanedicarboxylic acid was previously reported by Avdonin et al.[12] to be (−318.5 ± 12.6) kJ·mol^{-1}, a value which is less than that obtained in this work and outside the combined uncertainty limits. The combustion experiments reported by Avdonin et al. were performed without the use of auxiliary combustion aids.

Fusion Enthalpy. A typical DSC thermogram for 1,4-cubanedicarboxylic acid is presented in Figure 2. The material showed a broad endothermic transition from T = (443 to 493) K followed by a sharp endothermic transition with an onset temperature of 495 K, after which rapid exothermic decomposition occurred. The broad peak usually exhibited some fine structure, as illustrated in Figure 2. In all of the DSC experiments, the heating rate was maintained at 10 K·min^{-1}. In one experiment, the DSC was immediately cooled following the fusion transition. The presence of some 1,4-cubanedicarboxylic acid could be identified by analysis of the cooled residue using gas chromatography. The details of the DSC experiments are summarized in Table 3. The total phase-change enthalpy was obtained by extending a line from T = (443 to 498) K and measuring the resulting area. The baseline at T = 443 K was used as the first point of reference, and the minimun following the small peak at approximately T = 492 K was used as a second point of reference for integration. Since the peak at T = 492 K and the main fusion peak were not baseline-resolved, a point slightly below the minimum at T = 494 K was chosen, as shown in Figure 2. Since this reference point should be considered approximate, the fusion results must be considered as a qualitative evaluation of the total phase-change enthalpy of 1,4-cubanedicarboxylic acid. Therefore, the uncertainties reported are solely a measure of the reproducibility of the measurements. 1-Adamantanecarboxylic acid showed an endothermic transition only at the melting temperature over the temperature range T = (300 to 447) K.

Adjustment of the total phase-change enthalpy of 1,4-cubanedicarboxylic acid and the fusion enthalpy of 1-adamantanecarboxylic acid to T = 298.15 K was accomplished using eq 3:

$$\frac{\Delta C_p \cdot \Delta T}{\text{kJ} \cdot \text{mol}^{-1}} = \frac{((0.15C_{p,\,\text{cr}} - 0.26C_{p,\,\text{l}} - 9.83)\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(T_{\text{fus}} - 298.15\ \text{K})}{1000\ \text{J} \cdot \text{mol}^{-1}} \qquad (3)$$

This equation has been successfully used to adjust fusion enthalpies from T_{fus} to 298.15 K.[38] The symbols $C_{p,\text{l}}$ and $C_{p,\text{cr}}$ represent the heat capacities of the liquid and solid, respectively, which were estimated by group additivity;[30] the values are shown in Table 6. In this case, since the phase transitions occurring below the fusion temperature make a significant contribution to the total phase-change enthalpy, this equation is likely to somewhat

Table 6. Adjustment of the Total Solid−Liquid Phase-Change Enthalpy to T = 298.15 K

compound	$\Delta H_{\text{tpce}}(T_{\text{fus}})$ kJ·mol^{-1}	T_{fus} K	$C_{p,\text{l}}$ J·mol^{-1}·K^{-1}	$C_{p,\text{cr}}$ J·mol^{-1}·K^{-1}	$\Delta C_p \cdot \Delta T$ kJ·mol^{-1}	$\Delta H_{\text{tpce}}(298.15\ \text{K})$ kJ·mol^{-1}
1,4-cubanedicarboxylic acid	17.4 ± 1.2	495	334.4	188.6	−13.5 ± 4.0	4.0 ± 4.2
1-adamantanecarboxylic acid	16.2 ± 0.4[a]	447.2	322.6	241.9	−8.6 ± 2.6	7.6 ± 2.6

[a] Fusion enthalpy.

Table 7. Vaporization Enthalpies of 1,4-Cubanedicarboxylic Acid and 1-Adamantanecarboxylic Acid

Run A

	slope		$\Delta_{\mathrm{sln}}^{\mathrm{g}}H$(458 K)	$\Delta_{\mathrm{vap}}H$(298 K)/kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit	calcd
hexanedioic acid	−5654.5	13.074	47.01	105.2	106.5 ± 6.4
heptanedioic acid	−6210.2	13.861	51.63	112	112.4 ± 6.4
octanedioic acid	−6493.3	14.08	53.98	116.7	115.4 ± 6.5
nonanedioic acid	−6831.9	14.423	56.8	119.7	118.9 ± 6.5
decanedioic acid	−7250.4	14.946	60.28	124.8	123.3 ± 6.5
1,4-cubanedicarboxylic acid	−7275.4	15.613	65.74		123.6 ± 6.5
dodecanedioic acid	−7908.0	14.815	60.48	128.4	130.2 ± 6.6

$$\frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}(298.15\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}} = (1.265 \pm 0.107)\frac{\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}(458\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}} + (47.07 \pm 6.0);\quad r^2 = 0.9724 \tag{4}$$

Run B

	slope		$\Delta_{\mathrm{sln}}^{\mathrm{g}}H$(458 K)	$\Delta_{\mathrm{vap}}H$(298 K)/kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit	calcd
hexanedioic acid	−5594.6	12.945	46.51	105.2 ± 2.2	106.4 ± 8.5
heptanedioic acid	−6224.4	13.890	51.75	112.0 ± 0.8	112.8 ± 8.9
octanedioic acid	−6497.5	14.091	54.02	116.7 ± 0.8	115.6 ± 9.0
nonanedioic acid	−6793.6	14.346	56.48	119.7 ± 0.8	118.6 ± 9.3
decanedioic acid	−7212.6	14.869	59.96	124.8	122.9 ± 9.6
1,4-cubanedicarboxylic acid	−7067.5	14.373	58.76		121.4 ± 9.5
dodecanedioic acid	−7958.5	15.722	66.16	130	130.5 ± 10.0

$$\frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}(298.15\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}} = (1.223 \pm 0.116)\frac{\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}(458\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}} + (50.0 \pm 6.53);\quad r^2 = 0.9651 \tag{5}$$

Run C

	slope		$\Delta_{\mathrm{sln}}^{\mathrm{g}}H$(445 K)	$\Delta_{\mathrm{vap}}H$(298 K)/kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit	calcd
decanoic acid	−5864.2	12.764	48.75	90.3	89.8 ± 3.7
undecanoic acid	−6293.9	13.281	52.33	93.88	95.1 ± 3.8
1-adamantanecarboxylic acid	−5967.6	12.148	49.61		91.1 ± 3.7
dodecanoic acid	−6719.4	13.793	55.86	100.81	100.2 ± 3.9
tridecanoic acid	−7189.7	14.412	59.77	106.45	106.0 ± 4.0
tetradecanoic acid	−7663.2	15.035	63.71	111.38	111.8 ± 4.2
pentadecanoic acid	−8071.3	15.527	67.1	116.77	116.7 ± 4.3

$$\frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}(298.15\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}} = (1.467 \pm 0.049)\frac{\Delta_{\mathrm{sln}}^{\mathrm{g}}H_{\mathrm{m}}(445\ \mathrm{K})}{\mathrm{kJ\cdot mol^{-1}}} + (18.29 \pm 0.76);\quad r^2 = 0.9956 \tag{6}$$

overestimate the heat capacity correction. The uncertainty in the heat capacity correction was estimated to be 30 % of the correction.

Vaporization Enthalpy. The vaporization enthalpies of 1,4-cubanedicarboxylic acid and 1-adamantanecarboxylic acid were evaluated by correlation-gas chromatography using a series of alkanedioic acids and alkanoic acids as standards. Methanol was used as the solvent and nonretained reference for 1,4-cubanedicarboxylic acid, and methylene chloride was used in a similar role for 1-adamantanecarboxylic acid. The retention times measured for the two compounds are provided in the Supporting Information. The slopes and intercepts obtained from plots of $\ln(t_{\mathrm{o}}/t_{\mathrm{a}})$ versus

Table 8. Evaluation of the Sublimation Enthalpies of 1,4-Cubanedicarboxylic Acid and 1-Adamantanecarboxylic Acid

	$\Delta H_{\mathrm{tpce}}(298\ \mathrm{K})$	$\Delta H_{\mathrm{vap}}(298\ \mathrm{K})$	$\Delta_{\mathrm{vap}}H^{\circ}_{\mathrm{m}}(298\ \mathrm{K})_{\mathrm{avg}}$	$\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}(298\ \mathrm{K})$
compound	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
1,4-cubanedicarboxylic acid	3.95 ± 4.2		122.5 ± 8.0	126.5 ± 9.0
run A		123.6 ± 6.5		
run B		121.4 ± 9.5		
1-adamantanecarboxylic acid	7.6 ± 2.6	91.1 ± 3.7	91.1 ± 3.7	98.7 ± 4.5

Table 9. Experimentally Determined Thermodynamic Quantities at T = 298.15 K for 1-Adamantanecarboxylic Acid and 1,4-Cubanedicarboxylic Acid

	$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{cr})$	$\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}(298\ \mathrm{K})$	$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{g})$
compound	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
1-adamantanecarboxylic acid	−643.1 ± 3.8[a]	98.7 ± 4.5	−544.4 ± 5.9
1,4-cubanedicarboxylic acid	−355.9 ± 11.7	126.5 ± 9.0	−229.4 ± 14.8

[a] Value taken from ref 40.

$1/T$ for both the standards and the two acids are reported in the second and third columns of Table 7.

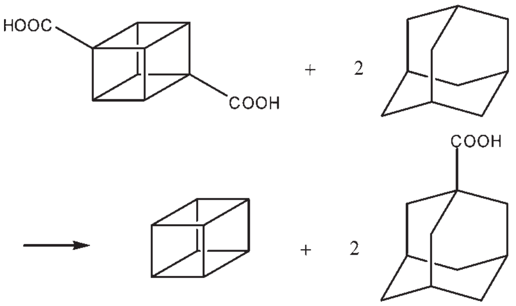
The vaporization enthalpies of the C_7—C_9 and C_{12} diacids used as standards were previously evaluated by correlation-gas chromatography using the literature values for the C_4, C_6, and C_{10} diacids as standards, and values at T = 298.15 K are available.[26] The vaporization enthalpies of the C_4, C_6, and C_{10} diacid standards were obtained as the differences between the corresponding sublimation enthalpy, $\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}(298\ \mathrm{K})$, and fusion enthalpy, $\Delta_{\mathrm{fus}}H^{\circ}_{\mathrm{m}}(298.15\ \mathrm{K})$. It should be noted that the vaporization enthalpy of dodecanedioic acid measured by correlation-gas chromatography is sensitive to the temperature of measurement and increases with increasing temperature. This sensitivity to the temperature of measurement has been interpreted as resulting from an equilibrium between a cyclized intramolecularly hydrogen-bonded structure and an acyclic form in the gas phase. The sublimation enthalpies of other alkanedioic acids of similar size show the same behavior.[39] The value used for the vaporization enthalpy of dodecanedioic acid at the mean temperature of these measurements, T_{m} = 458 K, is the value measured at the mean temperature, T_{m} = 459 K. Equations 4 to 6 provided below the data for the corresponding runs in Table 7 describe the quality the correlations.

Sublimation Enthalpy. The sublimation enthalpies of 1,4-cubanedicarboxylic acid and 1-adamantanecarboxylic acid can be calculated as the sums of the corresponding fusion and vaporization enthalpies, both evaluated at T = 298.15 K. Table 8 summarizes the sublimation enthalpies evaluated in this manner.

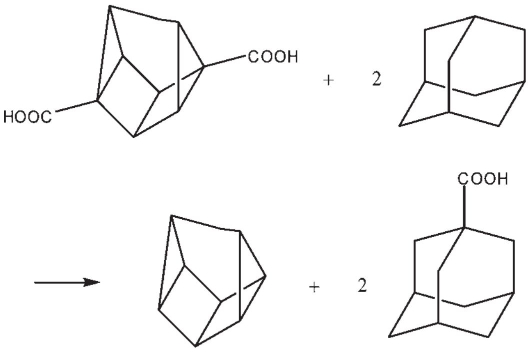
Gas-Phase Enthalpy of Formation. The gas-phase enthalpies of formation of 1,4-cubanedicarboxylic acid and 1-adamantanecarboxylic acid were calculated by combining the condensed phase enthalpies of formation [(−355.9 ± 11.7 and −643.1 ± 3.8) $\mathrm{kJ \cdot mol^{-1}}$, respectively] with the corresponding enthalpies of sublimation [(126.5 ± 9.0 and 98.7 ± 4.5) $\mathrm{kJ \cdot mol^{-1}}$, respectively]. The condensed-phase enthalpy of formation of 1-adamantanecarboxylic acid was previously reported by Steele et al.[40] The results are summarized in Table 9.

Theoretical Calculations. The results from the theoretical calculations at the MP2(Full)/6-31G(d) level for 1,4-cubanedicarboxylic acid, 2,6-cuneanedicarboxylic acid (whose experimental gas-phase enthalpy of formation is unknown), and 1-adamantanecarboxylic acid are shown in Table 10. Data for use in isodesmic reactions were taken from the following: for cubane and cuneane, ref 13; for 1-adamantanecarboxylic acid, Table 9 and the associated text as well as ref 41.

Theoretical values of the enthalpies of formation for 1,4-cubanedicarboxylic acid and 2,6-cuneanedicarboxylic acid studied in this work can be obtained using the following isodesmic reactions:



(7)



(8)

The theoretical calculations indicated that neither of these two reactions is exactly thermoneutral, gaving enthalpies of reaction of (6.8 and 22.2) $\mathrm{kJ \cdot mol^{-1}}$, respectively. Depending on the values taken for the enthalpies of formation of cubane and cuneane (see our previous paper[13]), different values of the enthalpies of formation can be obtained from the value for 1-adamantanecarboxylic acid given in the current study. Using

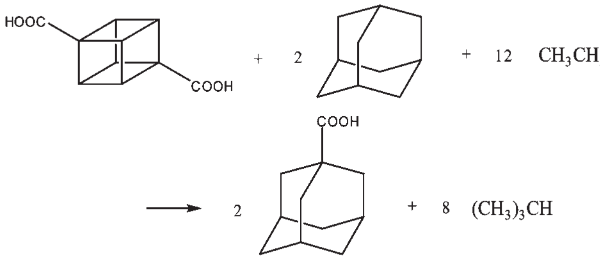
Table 10. MP2(FULL)/6-31G(d) Energies (E_{el}), Zero-Point Vibrational Energies (ZPE), Thermal Corrections to Enthalpies (TCH), and Enthalpies at 298 K (H_{298K}) for 1,4-Cubanedicarboxylic Acid, 2,6-Cuneanedicarboxylic Acid, and 1-Adamantanecarboxylic Acid (All Values in hartrees; 1 hartree = 2625.5 kJ·mol^{-1})

	E_{el}	ZPE[a]	TCH[a]	H_{298K}
1,4-cubanedicarboxylic acid	−684.675989	0.178001	0.188923	−684.502463
2,6-cuneanedicarboxylic acid	−684.750771	0.178675	0.189504	−684.576722
1-adamantanecarboxylic acid	−577.493479	0.277990	0.288155	−577.229370

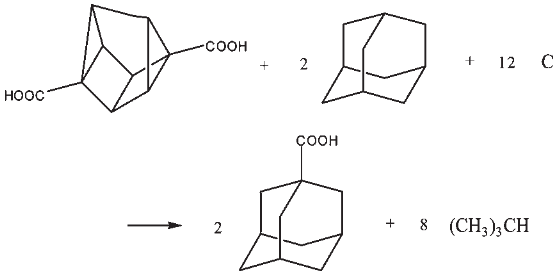
[a] Values were obtained at the HF/6-31G(d) level.

for the enthalpy of formation of cubane a value of (613.0 ± 9.5 or 602.7 ± 7.3) kJ·mol^{-1} affords a value of (−213.4 ± 13.0 or −223.7 ± 11.5) kJ·mol^{-1} for the enthalpy of formation of 1,4-cubanedicarboxylic acid,[41] in good agreement with the experimental value of (−229.4 ± 14.8) kJ·mol^{-1} measured in this work. Using for the enthalpy of formation of cuneane a value of (436.4 ± 8.8 or 441.2 ± 7.3) kJ·mol^{-1} gives a value of (−405.4 ± 12.5 or −400.6 ± 11.5) kJ·mol^{-1} for the enthalpy of formation of 1,4-cuneanedicarboxylic acid. Recent G4(MP2) quantum-chemical computations[42] gave the values (602.9 and 442.2) kJ·mol^{-1} for the enthalpies of formation of cubane and cuneane, respectively; we note that a plethora of values for cubane, generally unmatched by those of cuneane, have been calculated at both lower and higher computational levels.[43] We suggest a consensus value of (608 ± 13) kJ·mol^{-1} for the former (which is still a contentious number) to reflect uncertainties in the experimentally measured and theoretically calculated results.

Use of the following isodesmic reactions allows the strain energies to be estimated:

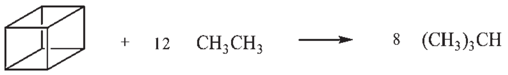


(9)



(10)

From theoretical calculations we obtained values of (678.5 and 483.6) kJ·mol^{-1} for the strain energies of 1,4-cubanedicarboxylic acid and 2,6-cuneanedicarboxylic acid, respectively. Using solely experimental enthalpies of formation afforded a value of (658.2 ± 17.4) kJ·mol^{-1} for the strain energy of 1,4-cubanedicarboxylic acid. For comparison, using the isodesmic reaction given by eq 11 and the consensus value for the enthalpy of formation of cubane gave a strain enthalpy of (676.0 ± 13.2) kJ·mol^{-1} for cubane, which is within the experimental error measured for the strain energy estimated for 1,4-cubanedicarboxylic acid. A strain energy of (674.2 ± 9.8) kJ·mol^{-1} was recently calculated for dimethyl 1,4-cubanedicarboxylate.[13] For the isomerization of 1,4-cubanedicarboxylic acid to 2,6-cuneanedicarboxylic acid, a theoretical isomerization enthalpy of −195.0 kJ·mol^{-1} was obtained. This can be compared to the value of (−190.9 ± 9.2) kJ·mol^{-1} evaluated from experimental $\Delta_f H_m^\circ$(g) values for isomerization of the corresponding dimethyl 1,4-cubanedicarboxylate.[13]



(11)

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Retention times from which the data in Table 7 were obtained. This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding Sources

The support of the Spanish Ministerio de Ciencia e Innovación under Projects CTQ2007-60895/BQU and CTQ2010-16402 is gratefully acknowledged.

Notes

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