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The enthalpies of vaporization and sublimation of *exo*- and *endo*-tetrahydrodicyclopentadienes at $T = 298.15\,\mathrm{K}$

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The vaporization enthalpies $\{\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}\ (298.15\,\mathrm{K})\}$ of *endo*- and *exo*-tetrahydrodicyclopentadiene (THDCPD) have been measured by correlation gas chromatography. Values of $(50.2 \pm 2.3)\,\mathrm{kJ \cdot mol^{-1}}$ and $(49.1 \pm 2.3)\,\mathrm{kJ \cdot mol^{-1}}$ have been obtained for the *endo* and *exo* isomers, respectively. The sublimation enthalpy of the *endo* isomer $\{\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\,\mathrm{K}) = (51.2 \pm 2.4)\,\mathrm{kJ \cdot mol^{-1}}\}$ has been obtained by combining fusion and vaporization enthalpies adjusted as necessary to $T = 298.15\,\mathrm{K}$. Low-temperature d.s.c. studies of both isomers reveal solid-to-solid phase transitions. The *endo* isomer, which is a plastic crystal at room temperature, exhibits a solid-to-solid phase transition at $T = 214\,\mathrm{K}$ $\{\Delta_{\mathrm{cr(2)}}^{\mathrm{cr(1)}}H_{\mathrm{m}}(214\,\mathrm{K}) = (10.7 \pm 0.13)\,\mathrm{kJ \cdot mol^{-1}}\}$ and a melting temperature of $356.8\,\mathrm{K}$ $\{\Delta_{\mathrm{cr(1)}}^{\mathrm{l}}H_{\mathrm{m}}(356.8\,\mathrm{K}) = (3.48 \pm 0.2)\,\mathrm{kJ \cdot mol^{-1}}\}$ with some evidence of polymorphism. The *exo* isomer exhibits a solid phase transition at $T = 162.1\,\mathrm{K}$ $\{\Delta_{\mathrm{cr(2)}}^{\mathrm{cr(1)}}H_{\mathrm{m}}(162.1\,\mathrm{K}) = (3.18 \pm 0.11)\,\mathrm{kJ \cdot mol^{-1}}\}$ and a melting temperature of $183.2\,\mathrm{K}$ $\{\Delta_{\mathrm{cr(1)}}^{\mathrm{l}}H_{\mathrm{m}}(183.2\,\mathrm{K}) = (1.20 \pm 0.04)\,\mathrm{kJ \cdot mol^{-1}}\}$. Enthalpies of vaporization and sublimation are combined with the respective enthalpies of formation previously reported to yield the following gas-phase values: for *endo* THDCPD, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0} = -(61.9 \pm 3.2)\,\mathrm{kJ \cdot mol^{-1}}$; and for *exo*-THDCPD, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0} = -(73.7 \pm 2.7)\,\mathrm{kJ \cdot mol^{-1}}$. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The *exo* isomer of tetrahydrodicyclopentadiene (*exo*-THDCPD) is the major component of the high-energy-density rocket fuel referred to as JP-10. The *endo* isomer (*endo*-THDCPD), which is the precursor of the *exo* isomer, is also present in JP-10 as a minor

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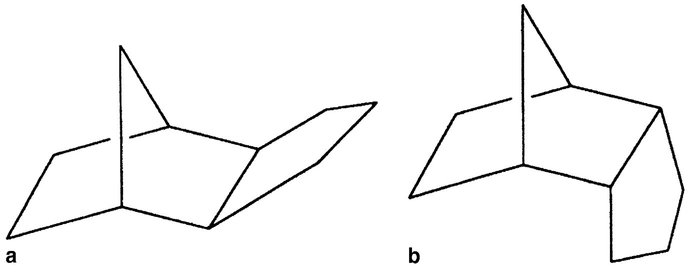

FIGURE 1. The structures of a, *exo*- and b, *endo*-tetrahydrodicyclopentadiene.

component.(1) Despite their importance, very little thermochemical information on the pure tricyclic isomers (figure 1) is available in the chemical literature. The enthalpy of formation of the pure *endo* isomer in the gas phase has been reported by Boyd *et al.*(2) The heat capacity, vaporization enthalpy at $T = 298.15$ K, and the fusion enthalpy of the *endo* isomer were also reported by these workers. The enthalpy of combustion of the *exo* isomer has been reported by Smith and Good(3) although the purity of the material burned was not given. Some additional physical properties of impure samples of *exo*-THDCPD have also been reported by Moynihan *et al.*(4) This work reports the enthalpies of fusion and vaporization of the pure *exo* and *endo* isomers as well as the heat capacity of the *exo* isomer from $T = 193.15$ K to $T = 273.15$ K.

Solid-to-solid transition enthalpies and enthalpies of fusion of *endo*- and *exo*-THDCPD have been measured by d.s.c. The sublimation enthalpy of the *endo* isomer has also been determined from the sum of the vaporization and fusion enthalpies adjusted to $T = 298.15$ K. The vaporization enthalpies of these samples have been obtained from correlation-gas chromatography.(5,6) On the basis of the previously measured enthalpies of combustion,(2,3) the gas-phase enthalpies of formation of the two isomers are compared with related measurements and estimates.

2. Experimental

Both *endo*- and *exo*-THDCPD were obtained as commercial samples from Koch Specialty Chemical. The *endo* isomer was purified by two recrystallizations from methanol. The *exo* isomer was purified by preparative gas chromatography on a Varian Aerograph Model 920 instrument equipped with a thermoconductivity detector on a 1 cm by 6 m, 30 percent SE 30 on Chromosorb W, column at a column temperature of 450 K. The purities of *endo*- and *exo*-THDCPD, as determined by capillary gas chromatography, were mass fractions 0.994 and 0.998, respectively. The structures of the purified materials were confirmed by ^{1}H n.m.r. and ^{13}C n.m.r. Correlation gas chromatography experiments were performed on an HP 5890 Series II gas chromatograph equipped with a split/splitless capillary injection port and a flame ionization detector. Retention times were recorded to three significant figures following the decimal point on a HP 3989A integrator. The instrument was run isothermally with a 12 m HP-1 capillary column. At the temperatures of the experiments, the solvent was not retained; the retention times of the solvent were used to determine the dead volume of the column. Corrected retention times t_{rc} were calculated by subtracting the measured retention time of each analyte from the retention time of the solvent as a function of temperature 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 to ±0.2 K. The purity of the commercially available standards generally had a mass fraction purity of 0.99 or greater. The purities of the standards are not particularly relevant since the chromatography generally separates the impurities. In addition, the standards and *endo*- and *exo*-THDCPD were analyzed as a mixture.

Fusion enthalpies and heat capacities were measured on a Perkin–Elmer DSC-7 equipped with a low-temperature heat exchange block, supplied by the manufacturer, that was cooled in liquid nitrogen. The sample cells were shielded from their environment by means of a Plexiglass dry box that was purged with dry nitrogen. Fusion measurements were performed under nitrogen at a temperature scan rate of $0.083\,\mathrm{K \cdot s^{-1}}$. The samples were hermetically sealed in stainless steel capsules. D.s.c. onset temperatures are reported as melting temperatures. Fusion and transition enthalpies of the *endo* and *exo* isomers were measured on sample sizes ranging from (25 to 30) mg and (15 to 20) mg, respectively. The instrument was standardized by using the fusion enthalpy of indium, and was checked against the fusion enthalpies of heptane, biphenyl, naphthalene, and benzoic acid.(11) The heat capacity of *exo*-THDCPD was measured from $T = 193.15\,\mathrm{K}$ to $T = 273.15\,\mathrm{K}$ relative to the values for heptane(7) and cyclopentane(8) at several scan rates. With cyclopentane, the heat capacity was measured repetitively with scan rates of $0.333\,\mathrm{K \cdot s^{-1}}$ over a 50 K range; with heptane, scan rates of $0.167\,\mathrm{K \cdot s^{-1}}$ and $0.033\,\mathrm{K \cdot s^{-1}}$ were used over temperature intervals of 30 K and 80 K, respectively. The solid to solid phase transition at $T = 162.1\,\mathrm{K}$ discussed below interfered with measurements below $T = 193.15\,\mathrm{K}$. Heat capacity measurements of the *exo* isomer were measured on sample sizes ranging from (12 to 25) mg.

Enthalpies of vaporization of the standards used in the correlation gas chromatography experiments were adjusted to $T = 298.15\,\mathrm{K}$, if necessary by means of equation (1):

$$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\,\mathrm{K}) = \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}\langle T\rangle + \{10.58\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}} + 0.26 \cdot C_{\mathrm{p,m}}(\mathrm{l})\} \cdot \{\langle T\rangle - 298.15\,\mathrm{K}\}. \quad (1)$$

Fusion enthalpies were adjusted to $T = 298.15\,\mathrm{K}$ by means of equation (2), according to the protocol described elsewhere.(12–14)

$$\begin{aligned}\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(298.15\,\mathrm{K}) = {} & \Delta_{\mathrm{cr}}^{\mathrm{l}}\mathrm{H}_{\mathrm{m}}(T_{\mathrm{fus}}) + \{0.75 \cdot \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \\ & + 0.15 \cdot C_{\mathrm{p,m}}(\mathrm{cr})\} \cdot \{T_{\mathrm{fus}} - 298.15\,\mathrm{K}\} \\ & - \{10.58\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}} + 0.26 \cdot C_{\mathrm{p,m}}(\mathrm{l})\} \cdot \{T_{\mathrm{fus}} - 298.15\,\mathrm{K}\}. \quad (2)\end{aligned}$$

The terms $C_{\mathrm{p,m}}(\mathrm{cr})$ and $C_{\mathrm{p,m}}(\mathrm{l})$ refer to the molar heat capacities of the solid and liquid phase at $T = 298.15\,\mathrm{K}$, respectively, and were estimated according to a group additivity

TABLE 1. Group values Γ, Δ, E used to estimate molar heat capacities, total phase change entropies, and strainless gas phase enthalpies of formation, respectively[a]

Group values	Term	$\Gamma(\mathrm{l})$	$\Gamma(\mathrm{cr})$	Δ	$E^{(18,20)}$
		$(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	$(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	$(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	$(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$
Cyclic secondary sp^3 CH$_2$	A	25.9	24.6		−21.46 (−20.6)
Cyclic tertiary sp^3 CH	B	20.6	11.7	−14.7	−9.04 (−7.9)

[a] Property values were calculated as $6 \cdot \mathrm{A} + 4 \cdot \mathrm{B}$: $C_{\mathrm{p,m}}(\mathrm{l}) = 237.6\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at $T = 298.15\,\mathrm{K}$; $C_{\mathrm{p,m}}(\mathrm{cr}) = 194.4\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at $T = 298.15\,\mathrm{K}$; and $\Delta_{\mathrm{f}}H_{\mathrm{m}}(\mathrm{g}, 298.15\,\mathrm{K}) = -165.0\,\mathrm{kJ \cdot mol^{-1}}(-155.6\,\mathrm{kJ \cdot mol^{-1}})$. The latter two values were obtained from two sets of group values reported by Engler *et al.*(18) and Benson,(20) respectively. The quantity ΔS_{m} was calculated as $33.4 \cdot N + 3.7 \cdot (R - 3 \cdot N) + 4 \cdot B$, where N and R refer to the number of ring atoms and rings, respectively.(9)

approach.(15) The group values $\Gamma^{(1)}$ used to estimate $C_{\mathrm{p,m}}$ for the liquid and solid, $\Gamma(\mathrm{cr})$ and the estimate are provided in table 1.

Uncertainties are reported as two standard deviations $(\pm 2 \cdot \sigma)$ unless noted otherwise. The uncertainties associated with the use of equation (2) are estimated at one-third the total temperature adjustment $(\pm 2 \cdot \sigma)$.

3. Results and discussion

D.s.c. plots of the results of the enthalpy of fusion measurements of both the *endo*- and *exo*-THDCPD are shown in figures 2 and 3, respectively. At $T = 298.15$, the *endo* isomer

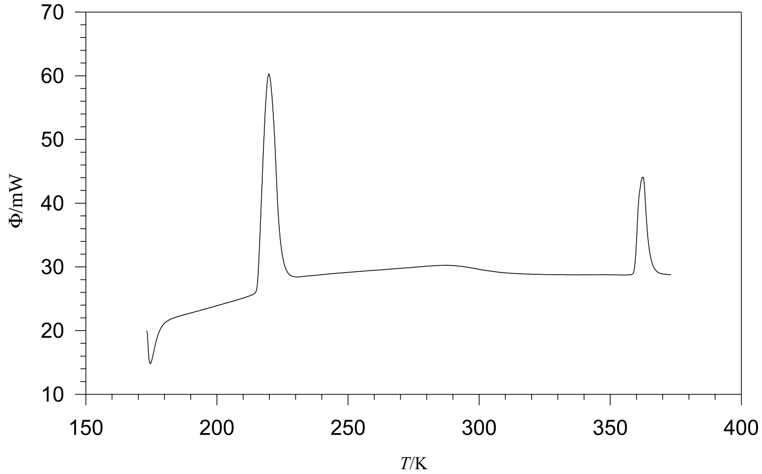

FIGURE 2. The d.s.c curve of *endo*-tetrahydrodicyclopentadiene. A plot of heat flow Φ against temperature. The small hump near $T = 273\,\mathrm{K}$ is probably due to water in the calorimeter and was not present in all scans.

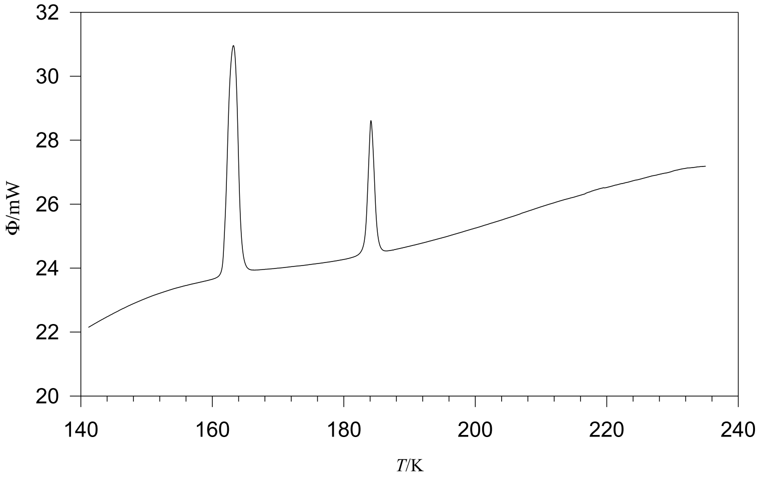

FIGURE 3. The d.s.c curve of *exo*-tetrahydrodicyclopentadiene. A plot of heat flow Φ against temperature.

behaves as a plastic crystal that melts at $T_{\mathrm{fus}} = 356.8\,\mathrm{K}$ with an enthalpy of fusion of $(3.48 \pm 0.2)\,\mathrm{kJ \cdot mol^{-1}}$ (scans I–IV, table 2). This compares with a value of $(2.95 \pm 0.04)\,\mathrm{kJ \cdot mol^{-1}}$ reported by Boyd *et al.*(2) A much larger transition for cr(2) = cr(1) is observed at $T = 213.8\,\mathrm{K}$. The enthalpy associated with this transition is $(10.7 \pm 0.13)\,\mathrm{kJ \cdot mol^{-1}}$. Some difference in melting temperature behavior was observed in comparing the value reported by Boyd *et al.* and the onset temperatures recorded by d.s.c. On further examination of this behavior, we observed that samples that were scanned from room temperature to the melting temperature (scans V and VI) behaved differently from those that were run from ≈173 K to the melting temperature (scans I to IV). The onset temperatures recorded by d.s.c. in scans V and VI (table 2) agree with the values reported by Boyd *et al.*(2) Differences were observed only when the samples were cooled first to low temperatures (scans I to IV). The observed melting temperatures appeared to be dependent on the thermal history of the sample, suggesting the possibility of polymorphism. Despite the differences in melting temperature, the enthalpies recorded remained constant. The mean fusion temperature and fusion enthalpy reported in table 2 were used in subsequent calculations.

The *exo* isomer, which is a liquid at room temperature, shows similar thermal behavior (scans VII to IX, table 2). A low-temperature solid-to-solid transition is observed at $T = 162.1\,\mathrm{K}$, and the compound melts at $T = 183.2\,\mathrm{K}$. The enthalpies associated with these two phase changes are considerably smaller: $(3.18 \pm 0.11)\,\mathrm{kJ \cdot mol^{-1}}$ and $(1.20 \pm 0.04)\,\mathrm{kJ \cdot mol^{-1}}$, respectively. Moynihan *et al.*(4) report $T_{\mathrm{fus}} = 182.4\,\mathrm{K}$ and a fusion enthalpy of $1.11\,\mathrm{kJ \cdot mol^{-1}}$ on a sample with a mass fraction purity of 0.968.

The total phase change entropies for the *endo* and *exo* isomers ΔS_{m} (table 2) are $59.9\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and $26.2\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively. The total phase change entropy estimated for the two compounds by group additivity (footnote a, table 1) is

TABLE 2. Molar enthalpies of fusion $\Delta^{\mathrm{l}}_{\mathrm{cr(2)}}H_{\mathrm{m}}$, transition $\Delta^{\mathrm{cr(2)}}_{\mathrm{cr(1)}}H_{\mathrm{m}}$, and total phase change entropies ΔS_{m} of *endo*- and *exo*-tetrahydrodicyclopentadiene

	T range/K	T_{trs}/K	T_{fus}/K	$\Delta^{\mathrm{cr(1)}}_{\mathrm{cr(2)}}H_{\mathrm{m}}(T_{\mathrm{trs}})$ $(\mathrm{kJ \cdot mol^{-1}})$	$\Delta^{\mathrm{l}}_{\mathrm{cr(1)}}H_{\mathrm{m}}(T_{\mathrm{fus}})$ $(\mathrm{kJ \cdot mol^{-1}})$	$\Delta S_{\mathrm{m}}{}^{a}$ $(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$
endo-tetrahydrodicyclopentadiene						
Scan I	173 to 373	215.4	354.4	10.9	3.71	
Scan II	173 to 373	214.2	359.1	10.6	3.38	
Scan III	173 to 373	215.6	359.4	10.7	3.36	
Scan IV	173 to 373	210.0	354.1	10.7	3.47	
Mean values:		213.8	356.8	10.7 ± 0.13	3.48 ± 0.2	59.9
ScanV	300 to 358		352.0		3.36	
Scan VI	300 to 358		351.6		3.41	
literature(2)			352		2.95 ± 0.04	
exo-tetrahydrodicyclopentadiene						
ScanVII		162.1	183.3	3.24	1.22	
Scan VIII		162.2	183.1	3.18	1.19	
Scan IX		162.1	183.2	3.12	1.18	
Mean values:		162.1 ± 0.1	183.2 ± 0.1	3.18 ± 0.11	1.20 ± 0.04	26.2
literature(11)			182.4		1.1	

[a] $\Delta S_{\mathrm{m}} = \Delta_{\mathrm{fus}}S_{\mathrm{m}} + \Delta_{\mathrm{trs}}S_{\mathrm{m}}$.

$45.1\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, about midway between the two values.(9) The lower value for the *exo* isomer suggests the possibility of additional phase changes at temperatures lower than those presently investigated.

The heat capacity of the *exo* isomer was measured from $T = 193.15\ \mathrm{K}$ to $273.15\ \mathrm{K}$. Table 3 compares the result of this study with those published previously by Moynihan *et al.*(4) The results are in good agreement. It was not possible to measure the heat capacity of cr(1) in the *exo* isomer below $T = 193\ \mathrm{K}$ by d.s.c. because of the proximity of the cr(2) = cr(1) transition. A three parameter fit of the results in table 3 is given by equation (3).

$$C_{\mathrm{p,m}}(\mathrm{l})_{\mathrm{exo}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 188.09 + 0.4697 \cdot (T/\mathrm{K}) + 9.10^{-5} \cdot (T/\mathrm{K})^{2}, \qquad (3)$$

with $r^{2} = 0.9734$.

Vaporization enthalpies were measured by correlation gas chromatography. Enthalpies of transfer from solution to the vapor were measured for both *endo*- and *exo*-THDCPD and an additional eight standards in three different mixtures. To test the reliability of the correlations, the vaporization enthalpies of both the *endo*- and *exo*-THDCPD were treated as unknowns. The retention times are reported in table 4, and the enthalpies of transfer from solution to the vapor, the vaporization enthalpy results, and the correlation

TABLE 3. Molar heat capacity $C_{\mathrm{p,m}}(\mathrm{l})$ of *exo*-tetrahydrodicyclopentadiene by d.s.c.; comparison with literature values

T/K	$C_{\mathrm{p,m}}(\mathrm{l})/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	
	This work[a]	Literature[b]34
193.15	153.1[c]	150.18
198.15	148.5[c]	152.69
203.15	157.9	155.20
213.15	161.2	160.21
223.15	165.1	165.23
233.15	169.0	170.24
243.15	172.7	175.26
253.15	180.6	180.28
263.15	182.0	185.29
273.15	188.6	190.31

[a] Mass fraction: 0.998, the reproducibility of the data was approximately ±6 percent.

[b] Mass fraction: 0.968.(4)

[c] Single determinations.

equations are reported in table 5. A typical plot of vaporization enthalpy against enthalpy of transfer from solution to the vapor is given in figure 4 for mixture 1.

Each enthalpy of transfer from solution to the gas phase reported in table 5 (column 2) was derived from the slope of the line obtained by plotting $\ln(s/t_{\mathrm{rc}})$ against $1/T$. The enthalpies of transfer of the standards measured over the temperature range reported in the table were then correlated with their respective enthalpies of vaporization at $T = 298.15\,\mathrm{K}$. The vaporization enthalpies calculated from the correlations, and their literature values, are reported in the third and fourth columns, respectively. Measurements were conducted over a range of temperatures. The mean temperature of measurement for each mixture, as well as the equation derived from each correlation, are reported in table 5. The uncertainties were generated from the standard error in the slope of the correlation equation.

Boyd *et al.*(2) measured the temperature dependence of vapor pressure for liquid *endo*-THDCPD with a glass Bourdon gauge nulled against a mercury manometer.(2) The vapor pressure results, $358 < (T/\mathrm{K}) < 417$, are given as equation (4):

$$\ln(p/\mathrm{kPa}) = -5235.4(\mathrm{K}/T) + 15.9. \tag{4}$$

A vaporization enthalpy of $(43.5 \pm 0.8)\,\mathrm{kJ \cdot mol^{-1}}$ at $\langle T \rangle = 387\,\mathrm{K}$ is obtained from equation (4) which, when adjusted to $T = 298.15\,\mathrm{K}$ by means of equation (1) results in a value of $(50.0 \pm 1.6)\,\mathrm{kJ \cdot mol^{-1}}$. This compares with a value of $(50.0 \pm 1.3)\,\mathrm{kJ \cdot mol^{-1}}$ obtained by subtracting the fusion enthalpy (at $T_{\mathrm{fus}} = 352\,\mathrm{K}$) from the sublimation enthalpy (at $T = 298.15\,\mathrm{K}$) reported in the Boyd *et al.* article. These two vaporization enthalpies are reported in the last two columns in table 6. The group values used to estimate the heat capacity of *endo*- and *exo*-THDCPD are reported in table 1, and the estimates used with equation (1) are reported in table 6. The temperature adjustment is

TABLE 4. Gas-chromatographic retention times t_r

T/K:		363.7	373.7	378.8	383.8	389.0	394.0	399.1	404.3
Mixture 1					t_r/s				
CH_2Cl_2		10.2	10.26	10.38	10.38	10.5	10.56	10.68	10.74
exo-THDCPD		63.84	49.14	43.26	38.46	34.8	31.68	29.04	26.76
Adamantane		70.62	54.12	47.58	42.18	38.04	35.34	30.6	28.26
endo-THDCPD		75.36	57.06	49.86	43.98	39.48	35.58	33	29.4
Naphthalene		115.8	84.54	72	62.04	54.84	48.3	43.2	38.46
n-Dodecane		151.92	104.64	86.82	72.9	63	54.18	47.64	41.46
Fluorene		1115.5	703.68	551.16	441.3	363.84	297.96	250.5	202.5
n-Hexadecane		2067.4	1194.3	902.1	692.88	548.88	431.88	350.22	274.26
T/K:	323.0	328.1	333.2	338.2	343.3	348.4	353.4	358.5	363.6
Mixture 2					t_r/s				
CH_2Cl_2	9.9	10.02	10.08	10.14	10.26	10.32	10.38	10.38	10.5
1-Octene	42.48	37.14	32.58	27.48	24.72	23.46	21.54	20.1	18.9
n-Nonane	95.82	79.56	66.42	53.58	46.92	41.04	35.52	32.04	29.22
t-Butylbenzene	170.64	139.32	114.42	90.96	77.1	66.3	55.62	49.44	44.4
exo-THDCPD	291.6	235.92	191.94	149.22	124.32	106.02	86.64	76.8	68.7
endo-THDCPD	361.62	290.22	234.36	181.74	150.24	126.9	103.26	90.6	80.4
Napthalene	642.54	505.02	400.86	303.3	245.82	204.48	162.6	140.4	123
Dodecane	1132.56	852.36	649.98	474.36	369.9	296.46	228.36	190.5	161.7
T/K:	333.3	338.3	343.4	348.4	353.5	358.6	363.7	368.8	373.9
Mixture 3					t_r/s				
CH_2Cl_2	10.8	10.86	10.98	11.04	11.1	11.16	11.34	11.4	11.46
n-Heptane	21.36	19.86	18.3	17.46	16.5	15.66	15.3	14.7	14.28
n-Nonane	68.04	57.42	47.94	41.82	36.24	32.04	28.74	25.8	23.82
exo-THDCP	188.64	154.2	124.62	104.7	87.12	74.04	63.84	54.78	48.54
endo-THDCP	229.2	186.12	149.76	124.8	103.2	87	74.4	63.6	55.86
n-Dodecane	644.16	493.56	373.5	295.26	230.34	184.26	149.82	120.72	101.82

included as the last entry under $\Delta C_{p,m}(l) \cdot \Delta T$ in table 6. Boyd *et al.*(2) used experimental condensed-phase heat capacities to adjust for temperature.

The results for both the vaporization and sublimation enthalpies obtained in this study are summarized in table 6 as are the values reported by Boyd *et al.*(2) Mean vaporization enthalpies of $(50.2 \pm 2.3)\,\mathrm{kJ \cdot mol^{-1}}$ and $(49.1 \pm 2.3)\,\mathrm{kJ \cdot mol^{-1}}$ were obtained for *endo*- and *exo*-THDCPD in this study, respectively. The uncertainties reported for both the *endo* and *exo* isomers represent two standard deviations of the mean of the values reported in table 6.

TABLE 5. Molar enthalpies of transfer from solution $\Delta_{\rm sln}^{\rm g}H_{\rm m}(\langle T\rangle)$ and enthalpies of vaporization $\Delta_{\rm l}^{\rm g}H_{\rm m}(298.15\,{\rm K})$ obtained by g.l.c. for mixtures 1 to 3

	$\Delta_{\rm sln}^{\rm g}H_{\rm m}(384\,{\rm K})$ / $({\rm kJ\cdot mol^{-1}})$	$\Delta_{\rm l}^{\rm g}H_{\rm m}(298.15\,{\rm K})^{a}$ / $({\rm kJ\cdot mol^{-1}})$	$\Delta_{\rm l}^{\rm g}H_{\rm m}(298.15\,{\rm K})^{b}$ / $({\rm kJ\cdot mol^{-1}})$
Mixture 1			
Adamantane	37.1	51.9 ± 2.3	52(12)
Naphthalene	40.2	55.7 ± 2.5	55.7(7)
n-Dodecane	45.9	62.7 ± 2.9	61.5(10)
Fluorene	52.4	70.7 ± 3.3	72.3(12)
n-Hexadecane	61.6	82.0 ± 3.8	81.4(10)
exo-THDCPD	36.4	51.0 ± 2.3	
endo-THDCPD	37.2	52.0 ± 2.3	
$\Delta_{\rm l}^{\rm g}H_{\rm m}(298.15\,{\rm K})/({\rm kJ\cdot mol^{-1}}) = (1.23 \pm 0.06)\cdot\Delta_{\rm sln}^{\rm g}H_{\rm m}(384\,{\rm K}) + (6.13 \pm 1.22), (r^2 = 0.9924)$			
Mixture 2			
1-Octene	32.8	41.3 ± 3.9	40.3(10)
n-Nonane	37.2	47.1 ± 4.4	46.6(10)
t-Butylbenzene	38.1	48.3 ± 4.5	49.3(11)
Napthalene	42.5	54.0 ± 5.0	55.7(7)
Dodecane	49.2	62.7 ± 5.8	61.5(10)
exo-THDCPD	38.9	49.3 ± 4.6	
endo-THDCPD	39.8	50.5 ± 4.7	
$\Delta_{\rm l}^{\rm g}H_{\rm m}(298.15\,{\rm K})/({\rm kJ\cdot mol^{-1}}) = (1.30 \pm 0.12)\cdot\Delta_{\rm sln}^{\rm g}H_{\rm m}(343.3\,{\rm K}) - (1.4 \pm 1.46), (r^2 = 0.9726)$			
Mixture 3			
n-Heptane	33.6	37.1 ± 3.0	36.6(10)
n-Nonane	39.3	47.1 ± 3.5	46.6(10)
n-Dodecane	49.9	62.1 ± 4.4	61.5(10)
exo-THDCP	40.2	47.1 ± 3.6	
endo-THDCP	40.8	48.03.6	
$\Delta_{\rm l}^{\rm g}H_{\rm m}(298.15\,{\rm K})/{\rm kJ\cdot Mol^{-1}} = (1.509 \pm 0.88)\cdot\Delta_{\rm sln}^{\rm g}H_{\rm m}(353.6\,{\rm K}) - (13.5 \pm 1.04), (r^2 = 0.9966)$			

The uncertainities $(\pm\sigma)$ were generated from the uncertainty associated with the slope of each correlation equation given at the bottom of each table. The correlation equations are listed below each mixture.

[a] Calculated.

[b] Taken from the literature.

Three values are reported in table 6 for the sublimation enthalpy of *endo*-THDCPD at $T = 298.15\,{\rm K}$. The first value was obtained from this study by combining the fusion enthalpy at $T = 298.15\,{\rm K}$ with the vaporization enthalpy also at $T = 298.15\,{\rm K}$. The second sublimation enthalpy was derived from the vaporization and fusion enthalpy data reported by Boyd *et al.*(2) adjusted to $T = 298.15\,{\rm K}$ by means of equations (1) and (2), and the third entry is the original value reported in the Boyd *et al.* article. The third entry

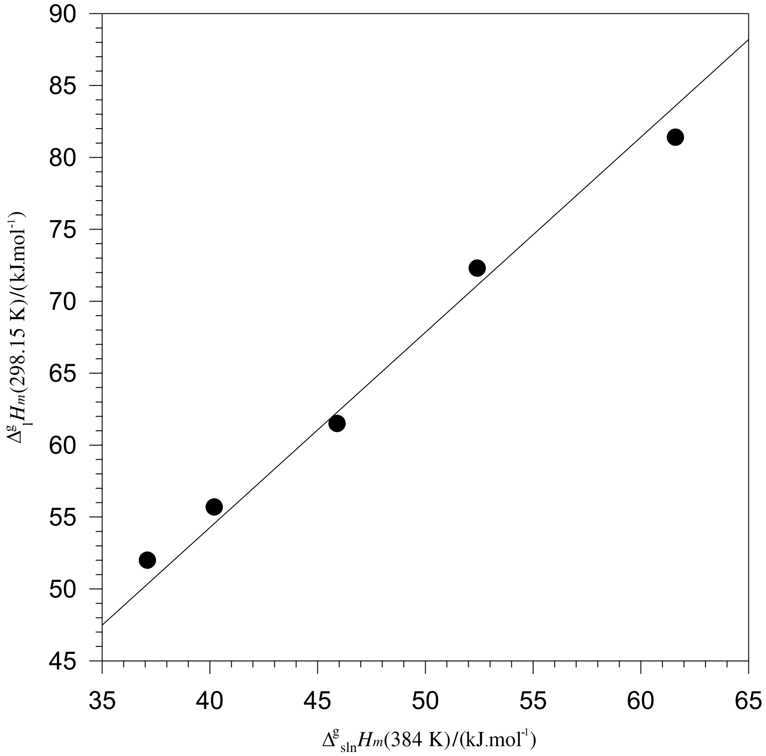

FIGURE 4. Correlation of $\Delta^{g}_{sln}H_m$ (343.3 K) with $\Delta^{g}_{l}H_m$ (298.15 K) for mixture 1.

was presumably obtained from the sum of the vaporization enthalpy at $T = 298.15$ K and the fusion enthalpy measured at $T = T_{fus}$. Despite different treatments, the agreement is still within the uncertainties cited. The mean value of the first two entries in table 6, (51.0 ± 2.0) kJ · mol^{-1}, is taken as the sublimation enthalpy of *endo*-THDCPD.

The enthalpies of combustion of both *endo*- and *exo*-THDCPD have been reported separately.(2,3) The results are summarized in the fourth column of table 7. Values of -393.51 kJ · mol^{-1} and -285.83 kJ · mol^{-1} for the enthalpies of formation of CO_2 (g) and H_2O (1),(16) respectively, combined with the enthalpies of combustion, result in standard molar enthalpies of formation of $-(112.9 \pm 2.5)$ kJ · mol^{-1} and $-(122.8 \pm 1.5)$ kJ · mol^{-1} for *endo*- (cr) and *exo*-THDCPD(1), respectively. When the sublimation enthalpy of *endo*-THDCPD is combined with the enthalpy of formation in the crystalline phase at $T = 298.15$ K, the enthalpy of formation in the gas phase, $-(61.9 \pm 3.1)$ kJ · mol^{-1}, is obtained. Similarly, the gas-phase enthalpy of formation of liquid *exo*-THDCPD is $-(73.7 \pm 3.4)$ kJ · mol^{-1}.

The difference in gas-phase enthalpies of formation, approximately 12 kJ · mol^{-1}, is consistent with the equilibrium studies of Schleyer and Donaldson(17) who found an *exo* to *endo* molar ratio of 99 to 1 at $T = 398$ K in the presence of catalytic amounts of

TABLE 6. A comparison of the molar enthalpies of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ and sublimation $\Delta_{\mathrm{cr(l)}}^{\mathrm{g}}H_{\mathrm{m}}$ at $T = 298.15\,\mathrm{K}$ obtained in this study with those reported by Boyd *et al.*(2)

	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}\langle T/\mathrm{K}\rangle$ / $(\mathrm{kJ\cdot mol^{-1}})$	$\langle T/\mathrm{K}\rangle$	$C_{\mathrm{p,m}}(\mathrm{l})$[a] / $\mathrm{J.K^{-1}\cdot mol^{-1}}$	$\Delta C_{\mathrm{p,m}}(\mathrm{l})\cdot\Delta T$[b] / $\mathrm{J.K^{-1}\cdot mol^{-1}}$	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\,\mathrm{K})$ / $(\mathrm{kJ\cdot mol^{-1}})$	
					This work	Literaure(2)
exo-THDCP			237.8 ± 15		49.1 ± 2.3[c]	
endo-THDCP					50.2 ± 2.3[c]	
endo-THDCP	43.5 ± 0.8(2)[d]	387.5	237.8 ± 15	6.5 ± 1.3	50.0 ± 1.6[e]	50.0 ± 1.3[d],[f]

	$\Delta_{\mathrm{cr(l)}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}})$ / $\mathrm{kJ\cdot mol^{-1}}$	$T_{\mathrm{fus}}/\mathrm{K}$	$C_{\mathrm{p,m}}(\mathrm{cr})$[a] / $(\mathrm{J\cdot K^{-1}mol^{-1}})$	$\Delta_{\mathrm{cr(l)}}^{\mathrm{l}}H_{\mathrm{m}}(298.15\,\mathrm{K})$ / $(\mathrm{kJ\cdot mol^{-1}})$	$\Delta_{\mathrm{cr(l)}}^{g}H_{\mathrm{m}}(298.15\,\mathrm{K})$ / $(\mathrm{kJ\cdot mol^{-1}})$
endo-THDCP	3.48 ± 0.23	356.8	194.4	1.0 ± 0.7	51.2 ± 2.4[c]
endo-THDCP(2)	2.95 ± 0.04	352	194.4	0.7 ± 0.7	50.7 ± 1.5[d]
endo-THDCP(2)					52.9 ± 1.3

[a] Estimated heat capacity at $T = 298.15$ K from table 1.(15)

[b] Calculated from the bracketed term in equation (1).

[c] This work.

[d] The uncertainity is an estimate.(2)

[e] Calculated from equation (4) as reported by Boyd *et al.*(2) and adjusted for temperature by means of equation (1).

[f] Calculated by subtracting the fusion enthalpy at $T = 352\,\mathrm{K}$ from the sublimation enthalpy at $T = 298.15\,\mathrm{K}$.(2)

TABLE 7. A comparison of molar enthalpies of combustion $\Delta_{\mathrm{c}}H_{\mathrm{m}}$ and formation $\Delta_{\mathrm{f}}H_{\mathrm{m}}$ of *endo*- and *exo*- tetrahydrodicyclopentadiene

	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\,\mathrm{K})$ / $(\mathrm{kJ\cdot mol^{-1}})$	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\,\mathrm{K})$ / $(\mathrm{kJ\cdot mol^{-1}})$	$\Delta_{\mathrm{c}}H_{\mathrm{m}}(298.15\,\mathrm{K})$ / $(\mathrm{kJ\cdot mol^{-1}})$
exo-THDCPD(l)	49.1 ± 2.3		−6098.9 ± 1.4(2)
endo-THDCP(cr(l))		51.0 ± 2.0	−6108.8 ± 2.5(3)

	$\Delta_{\mathrm{f}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\,\mathrm{K})$ / $(\mathrm{kJ\cdot mol^{-1}})$	$\Delta_{\mathrm{f}}H_{\mathrm{m}}(\mathrm{g}, 298.15\,\mathrm{K})$ / $(\mathrm{kJ\cdot mol^{-1}})$
exo-THDCPD(l)	−122.8 ± 2.5	−73.7 ± 2.7
endo-THDCP(cr(l))	−112.9 ± 2.5	−61.9 ± 3.2

aluminum chloride. This ratio translates to a Gibbs free energy difference of $-15.2\,\mathrm{kJ\cdot mol^{-1}}$. Assuming similar entropies for the two isomers, this difference approximates the differences observed thermochemically in the gas-phase enthalpies of formation at $T = 298.15\,\mathrm{K}$.

The last column in table 1 lists group values derived by Engler *et al.*(18) and by Benson;(20) Benson's values are given in parentheses. Estimated enthalpies of formation of strainless tetrahydrodicyclopentadiene of $-164.9\,\text{kJ}\cdot\text{mol}^{-1}$ and $-155.6\,\text{kJ}\cdot\text{mol}^{-1}$ are calculated, depending on which set of group values are used (footnote a of table 1). The differences between the experimental gas phase enthalpies of formation of both *exo*- and *endo*-THDCPD and these values implies strain enthalpies of $91.2\,\text{kJ}\cdot\text{mol}^{-1}$ and $103\,\text{kJ}\cdot\text{mol}^{-1}$ according to the Engler *et al.*(18) group values, and $81.9\,\text{kJ}\cdot\text{mol}^{-1}$ and $93.7\,\text{kJ}\cdot\text{mol}^{-1}$ according to Benson's(20) group values, respectively. The Engler *et al.* values compare favorably with strain energies of $94.8\,\text{kJ}\cdot\text{mol}^{-1}$ and $113.4\,\text{kJ}\cdot\text{mol}^{-1}$ calculated by molecular mechanics.(18,19) The strain enthalpies evaluated in these studies can be useful in assessing the enthalpy of formation of components of RJ-4, another high-energy-density rocket fuel, which is a complex mixture of *exo*- and *endo*-dimethyltetrahydrodicyclopentadiene isomers.

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