The enthalpies of combustion and formation of [2.2]-paracyclophane and triptycene

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The enthalpies of combustion, ΔH_c°, for crystalline [2.2]-paracyclophane ($C_{16}H_{16}$) and triptycene ($C_{20}H_{14}$) have been measured by oxygen combustion calorimetry. The derived standard enthalpies of formation at 298.15 K in the crystalline state are (34.59±0.19) and (51.87±0.20) $kcal_{th}\,mol^{-1}$. The strain present in these molecular systems is discussed.

1. Introduction

The macrocyclic hydrocarbon [2.2]-paracyclophane ($C_{16}H_{16}$, cyclo-di-*p*-xylylene, figure 1) is of thermodynamic interest since geometrical constraint[1–3] distorts the planarity of the aromatic rings and may engender strain relief by conformational
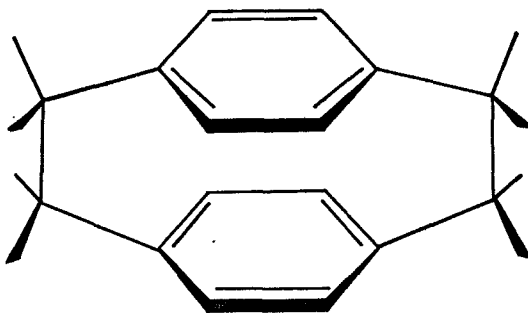

FIGURE 1. Paracyclophane.

twist.[3–5] Although a value for the enthalpy of combustion, ΔH_c°, for [2.2]-para-cyclophane has been reported[6] and the strain in the system apportioned between component contributions, the availability of a well-characterized sample for which thermal measurements have been reported,[4] permitted independent redetermination of the thermochemical properties and strain for this system. Determination of the

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thermochemistry for triptycene ($C_{20}H_{14}$, 9,10-*o*-benzeno-9,10-dihydroanthracene, figure 2) was undertaken to provide a better basis for interpreting the strain in the parent [2.2.2]-bicyclo-octane system.[7]
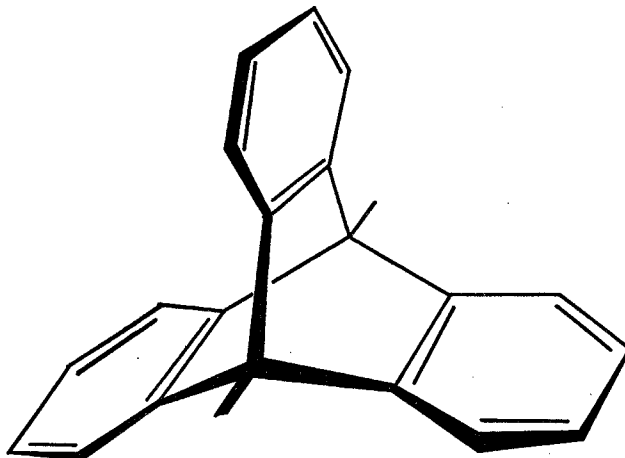
FIGURE 2. Triptycene.

2. Experimental

MATERIALS

Samples of both substances were purified by previously described techniques.[4, 8] [2.2]-Paracyclophane, which polymerizes readily above 410 K, was purified by a series of six vacuum sublimations; triptycene was purified by zone-melting, and fractional-fusion experiments indicated 0.001 mole per cent liquid-soluble solid-insoluble impurity.[8, 9]

CALORIMETRIC PROCEDURE

The calorimetric system has been described in detail elsewhere.[10] Both samples were burned as pellets in a baffle-covered platinum crucible and were ignited by measured discharge of electrical energy and unmercerized cotton fuse (empirical formula $CH_{1.686}O_{0.843}$, $-\Delta E_c^\circ/M = 4108 \, cal_{th} \, g^{-1}$).† Bomb rotation was initiated at the mid-point of the temperature rise and was continued throughout the remainder of the calorimetric experiment. Temperatures were measured with stainless-steel-sheathed platinum-resistance thermometers and a G-2 Müller bridge. After each experiment, the bomb solution was titrated with 0.01 mol dm^{-3} sodium hydroxide in the presence of methyl orange indicator to determine the nitric acid equivalent.[11] Data reduction and correction to standard state conditions were performed by digital computer.

† Throughout this paper $cal_{th} = 4.184 \, J$.

CALIBRATION

National Bureau of Standards benzoic acid, sample 39i, $-\Delta E_c^\circ/M = (26434.0 \pm 3.3)$ $J\,g^{-1}$,[12] was used to determine the energy equivalent of the calorimetric system. For triptycene, the bomb (laboratory designation NR-2) had an internal volume $0.3520\,dm^3$ and the energy equivalent of the system (Series I) based upon five determinations (3992.65, 3992.82, 3992.92, 3993.05, 3993.35), yields an average value $(3992.96 \pm 0.24)\,cal_{th}\,K^{-1}$. The precision index is twice the overall standard deviation[13] of the mean value. For [2.2]-paracyclophane, the internal volume of the same bomb was $0.3517\,dm^3$ and the energy equivalent of the system (Series II) based upon five determinations (3995.05, 3995.08, 3995.20, 3995.10, 3995.27) yields an average value $(3995.14 \pm 0.08)\,cal_{th}\,K^{-1}$ with similarly defined precision index.

UNITS AND AUXILIARY QUANTITIES

The 1962 scale of atomic weights[14] was used and the ice point was taken as 273.15 K. The values for parameters used to correct standard state conditions are given in table 1 and were obtained from the literature, or estimated from those of similar

TABLE 1. Values of density ρ, specific heat capacity c_p, and temperature coefficient of specific volume, $(\partial v/\partial T)_p$

$(cal_{th} = 4.184\,J)$

Substance	$\dfrac{\rho}{g\,cm^{-3}}$	$\dfrac{c_p}{cal_{th}\,K^{-1}\,g^{-1}}$	$\dfrac{10^6 (\partial v/\partial T)_p}{dm^3\,K^{-1}\,g^{-1}}$
[2.2]-Paracyclophane	1.229	0.290	0.50 [a]
Triptycene	1.227	0.266	0.72 [b]

[a] Estimated value.
[b] Estimated value for [2.2.2]-bicyclo-octane.[7]

materials. Enthalpies of formation, ΔH_f°, for $CO_2(g)$ and $H_2O(l)$ were the recommended values $-(94.051 \pm 0.010)\,kcal_{th}\,mol^{-1}$,[15, 16] and $-(68.315 \pm 0.010)\,kcal_{th}\,mol^{-1}$.[16]
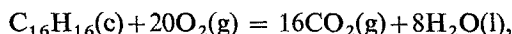
3. Results and discussion

CALORIMETRIC RESULTS

Eight combustions on paracyclophane and six combustions on triptycene were used to compute average values for $-\Delta E_c^\circ/M$ and the derived quantities. Results from typical combustions for each substance are summarized in table 2. The results of the individual combustion experiments, in terms of $-\Delta E_c^\circ/M$ at 298.15 K are: [2.2]-paracyclophane: 10002.93, 10000.95, 10001.95, 10002.95, 10000.89, 10003.34, 10002.22, 10004.47 $cal_{th}\,g^{-1}$; average value: $(10002.45 \pm 0.77)\,cal_{th}\,g^{-1}$; triptycene: 9472.37, 9472.65,

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TABLE 2. Results of typical combustion experiments

$(cal_{th} = 4.184 J)$

Compound	[2.2]-Paracyclophane	Triptycene
m'(sample)/g	0.667081	0.697968
m''(fuse)/g	0.001767	0.001694
$m'(H_2O)$/g	1.06	1.06
T_i/K − 273.15	23.27322	23.28671
T_f/K − 273.15	24.97205	24.97015
ΔT_c/K	1.68994	1.67559
$\Delta E_{ign}/cal_{th}$	0.27	0.28
ΔE(Washburn corr.)/cal_{th}	2.76	3.33
$\Delta E_{dec}(HNO_3)/cal_{th}$	0.97	0.96
$\Delta E_{soln}(CO_2)/cal_{th}$	0.64	0.64
$\Delta E_{diln}/cal_{th}$	0	0
$m''(\Delta E_c^\circ/M)$(fuse)/cal_{th}	7.26	6.96
$(\Delta E_c^\circ/M)$(sample)/$cal_{th} g^{-1}$	10001.95	9472.13

9472.65, 9471.89, 9470.91, 9471.71 $cal_{th} g^{-1}$; average value: $(9472.02 \pm 0.66) cal_{th} g^{-1}$, and refer to the reaction:

$$C_{16}H_{16}(c) + 20O_2(g) = 16CO_2(g) + 8H_2O(l),$$

for [2.2]-paracyclophane, and

$$C_{20}H_{14}(c) + 23.5O_2(g) = 20CO_2(g) + 7H_2O(l)$$
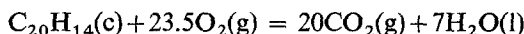
for triptycene.

4. Derived results

Average values for derived thermodynamic quantities at 298.15 K are summarized in table 3. The values $\Delta H_f^\circ(c)$, $\Delta S_f^\circ(c)$, and $\Delta G_f^\circ(c)$ are derived from the measured-values, the recommended values[16] for $\Delta H_f^\circ(CO_2, g)$, $\Delta H_f^\circ(H_2O, l)$, S°(graphite), $S^\circ(H_2, g)$, and the recently published values[3, 9] of S° for the compounds. Boyd's preferred

TABLE 3. Derived quantities

$(cal_{th} = 4.184 J)$

	Paracyclophane	Triptycene
$\Delta E_c^\circ(c)/kcal_{th} mol^{-1}$ [a]	− 2083.57 ± 0.15	− 2409.06 ± 0.28
$\Delta H_c^\circ(c)/kcal_{th} mol^{-1}$	− 2085.94 ± 0.15	− 2411.13 ± 0.28
$\Delta H_f^\circ(c)/kcal_{th} mol^{-1}$	34.59 ± 0.21	51.90 ± 0.30
$\Delta S_f^\circ(c)/cal_{th} K^{-1} mol^{-1}$	− 207.96 ± 0.10	− 180.22 ± 0.12
$\Delta G_f^\circ(c)/kcal_{th} mol^{-1}$	96.60 ± 0.20	105.60 ± 0.22
ΔH_v°(298.15 K)/$kcal_{th} mol^{-1}$	23 ± 1 [b]	25 ± 3 [c]
$\Delta H_f^\circ(g)/kcal_{th} mol^{-1}$	57.6 ± 1	76.9 ± 3

[a] Precision index as previously defined.

[b] Compare reference 6.

[c] We are indebted to Dr. Melvin Neuman of Dow Chemical Company for an estimate of the enthalpy of sublimation for triptycene in advance of publication.

value $-(2088.2\pm0.9)$ kcal$_{th}$ mol^{-1} for $\Delta H_c^\circ(c)$ for paracyclophane[6] differs somewhat from the present value $-(2085.94\pm0.16)$ kcal$_{th}$ mol^{-1}; no value for triptycene has been reported.

5. Discussion

A reference value, $\Delta H_f^\circ(g, \text{ref.})$, can be calculated for [2.2]-paracyclophane by the method of group increments,[18] which accounts for bond energies and substituent group interactions but ignores the energetic effects of molecular distortion. This value, 28.2 kcal$_{th}$ mol^{-1}, when compared with the experimental value, 57.6 kcal$_{th}$ mol^{-1}, suggests that the total strain energy in [2.2]-paracyclophane is approximately 29 kcal$_{th}$ mol^{-1}. The origin of this sizeable strain energy seems to rest with [2.2]-paracyclophane's distorted geometry, the consequences of which is the dishing of the benzene rings, and the elongation of the bridging bonds, all of which are obvious features of the X-ray structure.[1, 2]

Another procedure for obtaining a qualitative estimate of the total strain energy, first suggested by Boyd,[6] involves comparison of the enthalpy of hydrogenation of [2.2]-paracyclophane with that for the symmetrical cleavage of 1,2-diphenylethane under similar conditions. The results, together with an estimate for the total strain energy are summarized in table 4. As is readily seen, the results by the different methods are in reasonable accord and compare favorably with an *a priori* estimate, 33 kcal$_{th}$ mol^{-1}, by Trueblood (compare reference 6).

In Boyd's analysis,[6] the 4 kcal$_{th}$ mol^{-1} of total strain energy in paracyclophane which he assigns to eclipsed-hydrogen interactions may need downward revision in light of the observation made by some of us[4, 8] that there appears to be an anomaly in the low-temperature heat capacity at 50 K which suggests the possibility of strain relief by twisting. In the twisted conformation, the contribution of eclipsed-hydrogen interactions to the total strain energy in the molecule would tend to be reduced. Additional support for the "twist" conformation can be found in recent spectroscopic[5] and X-ray results.[3] For [2.2.2]-bicyclo-octane, where the skeleton is rigid, this mode of strain relief is not observed[20] and, therefore, eclipsed-hydrogen interactions make a full contribution to the total strain energy in the system.

The strain energy in triptycene may be evaluated in an analogous manner. The reference value $\Delta H_f^\circ(g, \text{ref.})$ calculated by group increments gives 70.2 kcal$_{th}$ mol^{-1} and a comparison with the experimental value 76.8 kcal$_{th}$ mol^{-1} suggests that the total strain energy in triptycene is approximately 7 kcal$_{th}$ mol^{-1}. The "direct comparison" method, involving in each case, hydrogenation of three carbon—hydrogen bonds to three phenyl—hydrogen bonds is illustrated in table 5. That the reaction for triptycene is more energetic suggests that triptycene is, in fact, strained. Once again, the magnitude of total strain energy by independent methods is within reasonable accord and within the uncertainty imposed by lack of an experimental value for the enthalpy of vaporization, ΔH_v°, for triptycene at 298.15 K.

In bicyclo-[2.2.2]-octane, the contribution of angular strain is a minor component to the total strain energy; most of the strain has its origin in the three eclipsed-hydrogen interactions.[7, 21] Triptycene may be presumed to be a rigid structure

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TABLE 4. Strain energy E_{strain} in [2.2]-paracyclophane at 298.15 K by direct comparison (compare references 18 and 19)
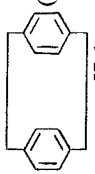
($cal_{th} = 4.184$ J)

[structure] (g) + 2H_2(g) = 2CH_3— [benzene] —CH_3(g)

$\Delta H_r^\circ = -49.0$ kcal$_{th}$ mol^{-1}

ΔH_f°(g)/kcal$_{th}$ mol^{-1}: 57.6 0 4.31

2 [benzene]—CH_2—CH_2 [structure] (g) + 2H_2(g) = 4 [benzene] —CH_3(g)

$\Delta H_r^\circ = -16.8$ kcal$_{th}$ mol^{-1}

ΔH_f°(g)/kcal$_{th}$ mol^{-1}: 32.4 0 11.99

$E_{strain} = \{-16.8 - (-49.0)\}$ kcal$_{th}$ mol$^{-1} - RT = 31.4$ kcal$_{th}$ mol^{-1}

TABLE 5. Strain energy E_{strain} in triptycene at 298.15 K by direct comparison (compare references 18 and 19)

($cal_{th} = 4.184$ J)

Triptycene(g) + 3H_2(g) = CH_4(g) + [benzene]_3CH(g)

$\Delta H_r^\circ = -29.9$ kcal$_{th}$ mol^{-1}

ΔH_f°(g)/kcal$_{th}$ mol^{-1}: 76.8 0 -17.89 64.8

[benzene]_3CH(g) + 3H_2(g) = CH_4(g) + 3 [benzene] (g)

$\Delta H_r^\circ = -23.3$ kcal$_{th}$ mol^{-1}

ΔH_f°(g)/kcal$_{th}$ mol^{-1}: 64.8 0 -17.89 19.81

$E_{strain} = \{-23.3 - (-29.9)\}$ kcal$_{th}$ mol$^{-1} - 2RT = 5.4$ kcal$_{th}$ mol^{-1}

devoid of eclipsed-hydrogen interactions if we adopt the suggestion that transannular interactions[22] and partial bond fixation[23] make a negligible contribution to the ground state. By analogy with 1-bromotriptycene[24] and β-bromo-1-ethyl triptycene,[25] the origin of the strain in triptycene must reside in the bicyclo-octane system as a result of the angular distortion between the bridgehead carbon atoms and the aromatic moieties.

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