Communications to the Editor

Formation Enthalpy of Corannulene: Microbomb Combustion Calorimetry[1]

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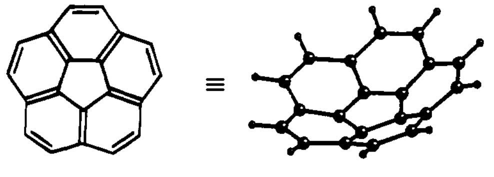
The remarkable yield of fullerenes and carbon nanotubes in arc discharge experiments has raised fundamental questions about the stability of nonplanar polycyclic aromatic hydrocarbons (PAHs) and carbon sheets. Enthalpies of formation of such systems provide the best quantitative measures of the thermodynamic stabilities they enjoy and the strains from which they suffer; however, experimental data in this area remain sparse. Corannulene (**1**), a bowl-shaped $C_{20}H_{10}$ hydrocarbon, represents the minimum fragment of a fullerene that retains the characteristic curvature. Herein we report our results from microbomb combustion calorimetry on corannulene and the first experimentally-based enthalpy of formation for this key compound.



Corannulene, 1

The original synthesis of corannulene, reported by Barth and Lawton in 1966,[5] gave sufficient quantities of **1** for X-ray analysis and for a variety of spectroscopic studies but not enough for calorimetric research. Fortunately, new synthetic strategies have finally made corannulene available in significantly larger quantities.[6] For the work described here, corannulene was prepared by flash vacuum pyrolysis of 7,10-bis(1-chlorovinyl)-fluoranthene.[6d,e] Material obtained in this manner, though pure by ^{1}H NMR spectroscopy, was shown by capillary GC/MS and analytical HPLC to contain trace amounts of chlorocorannulene, a contaminant formed in the pyrolysis. Repeated chromatography on silica gel and recrystallization ultimately gave pure hydrocarbon **1**.

Table 1. Standard Thermodynamic Quantities of Corannulene at 298.15 K

$\Delta_c u°(c)/J{\cdot}g^{-1}$	−38496 ± 22
$\Delta_c U°(c)/kJ{\cdot}mol^{-1}$	−9635.5 ± 5.4
$\Delta_c H°(c)/kJ{\cdot}mol^{-1}$	−9641.7 ± 5.4
$\Delta_f H°(c)/kJ{\cdot}mol^{-1}$	342.3 ± 5.6
$\Delta_{sub} H°/kJ{\cdot}mol^{-1}$	121.4[a]
$\Delta_f H°(g)/kJ{\cdot}mol^{-1}$	463.7

[a] Estimated by considering the empirical atom−atom potential in ref 10 and the crystal structure in ref 11.

Table 2. Comparison of Experimental (Boldface) and Theoretical Formation Enthalpies ($kJ{\cdot}mol^{-1}$)

	$C_{20}H_{10}$	C_{60}	C_{70}
$\Delta_f H°(c)$		**2327 ± 17**[a]	**2555 ± 12**[a]
		2278 ± 14[b]	
		2422 ± 14[c]	
	342.3 ± 5.6[d]	**2273 ± 15**[e]	**2375 ± 18**[e]
$\Delta_{sub} H°$	121.4[f]	**228.7 ± 7.3**[g]	**266.8**[h]
$\Delta_f H°(g)$	**463.7**[i]	**2501 ± 17**[i]	**2642**[i]
6-31G*	490.4[j]	2811.6[k]	
3-21G	504.2[j]		
STO-3G	516.3[j]		
PM3	584.5[l]	3396[l]	3699[l]
AM1	655.0[d]	4072[m]	4485[m]
MNDO	561.8[d]	3640[n]	3954[n]
MM2	460.7[o]	2175[p]	2438[p]
MM3	503.5[o]	2401[q]	
additivity	459.6[r]	2653[r]	2714[r]

[a] Reference 14a. [b] Reference 14b. [c] Reference 14c. [d] The present work. [e] Reference 14d. [f] Estimated by considering the empirical atom−atom potential in ref 10 and the crystal structure in ref 11. [g] Determined by Diogo et al. (ref 14b) with some experimental values cited therein. [h] Assumed to be $(70/60)\Delta_{sub}H(C_{60})$. [i] Used the values of $\Delta_f H°(c)$ in the fourth row of this table. [j] Schulman, J. M.; Peck, R. C.; Disch, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5675−5680. [k] Schulman, J. L.; Disch, R. L. *J. Chem. Soc., Chem. Commun.* **1991**, 411−412. [l] Matsuzawa, N.; Dixon, D. A. *J. Phys. Chem.* **1992**, *96*, 6241−6247. [m] Rudziński, J. M.; Slanina, Z.; Togasi, M.; Ōsawa, E.; Iizuka, T. *Thermochim. Acta* **1988**, *125*, 155−162. [n] Newton, M. D.; Stanton, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 2469−2470. [o] Allinger, N. L.; Nevins, N.; Lii, J.-H. Personal communication. [p] Froimowitz, M. J. *Comput. Chem.* **1991**, *12*, 1129−1133. [q] Diederich, F.; Whetten, R. L.; Thilgen, C.; Ettl, R.; Chao, I.; Alvarez, M. M. *Science* **1991**, *254*, 1768−1770. [r] Reference 15.

Details of the calorimeter used in this study will be described elsewhere.[7] The single valve microbomb of the calorimeter is equipped with a small platinum internal heater under the combustion crucible. Complete combustion is achieved by supplying electric energy to the internal heater during combustion. Electric current and voltage for heating were measured to be fed into transient memories. The energy equivalent of the empty calorimeter and a correction factor for the measured electric energy supplied to the internal heater were determined by burning 20 mg of thermochemical standard benzoic acid (NIST SRM 39i; $\Delta_c u_{cert} = -26434\ J{\cdot}g^{-1}$) under certificate conditions. The mean and standard deviation of the observed energy equivalents was 1378.94 ± 0.27 $J{\cdot}K^{-1}$ from six calibration runs. The correction factor for the measured electric energy was determined to be 0.998 97 ± 0.000 17.

The corannulene sample was formed into ~14 mg pellets for each combustion and burned under an oxygen pressure of 3.04 MPa in the presence of 24 mg of water in the microbomb with an internal volume of 9 cm^3. On each combustion run,

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90 J of electric energy was supplied to the internal heater to achieve complete combustion. No carbon soot was detected by visual observation of the crucible. No carbon monoxide was detected from the bomb gas after combustion. The amount of nitric acid, which was formed by the oxidation of nitrogen impurity contained in the oxygen gas, was determined by UV spectrometry of the bomb solution. The contribution of enthalpies of formation and solution of the nitric acid to the calorimetry were taken into account. The density and specific heat capacity of corannulene were taken to be 1.31 $\mathrm{g \cdot cm^{-3}}$ due to the crystal structure given in ref 11 and 1.045 $\mathrm{J \cdot K^{-1} \cdot g^{-1}}$, respectively, for the buoyancy correction and the reduction of the experimental results to the standard state values. Standard specific energy of combustion, $\Delta_c u°$, of polyethylene fuse was $-46305\ \mathrm{J \cdot g^{-1}}$.

Derived results of six experiments are as follows : $-\Delta_c u°(C_{20}H_{10})/\mathrm{J \cdot g^{-1}}$ = 38 487.1, 38 473.9, 38 508.2, 38 503.4, 38 523.4, and 38 480.3. The mean value and standard deviation is $-38\,496.0 \pm 7.6\ \mathrm{J \cdot g^{-1}}$. Standard thermodynamic quantities of corannulene are shown in Table 1. Reduction to standard state was carried out according to the literature procedure.[8] The values of $\Delta_c U°(c)$ and $\Delta_f H°(c)$ refer to the following reactions, respectively:

$$C_{20}H_{10}(c) + 22.5O_2(g) \rightarrow 20CO_2(g) + 5H_2O(l)$$

$$20C(\text{graphite}) + 5H_2(g) \rightarrow C_{20}H_{10}(c)$$

For calculation of $\Delta_f H°(c)$ value, the CODATA recommended standard formation enthalpies of $CO_2(g)$ ($-393.51 \pm 0.13\ \mathrm{kJ \cdot mol^{-1}}$) and of $H_2O(g)$ ($-285.830 \pm 0.042\ \mathrm{kJ \cdot mol^{-1}}$) were used.[9] Uncertainties are twice the final overall standard deviation of the mean according to the rule of error propagation.

In order to obtain the formation enthalpy in the gaseous state, we must determine the sublimation enthalpy. So far, no experimental value of the sublimation enthalpy of corannulene has been available. In Table 1, we show the sublimation enthalpy estimated by using an empirical nonbonded atom–atom potential proposed by Williams[10] on the basis of the crystal structure determined by X-ray diffraction.[11] We also estimated the contribution of dipole–dipole interaction to sublimation enthalpy with the dipole moment 2.433 D calculated with MOPAC v. 6.03 with the PM3 Hamiltonian.[12] Although this magnitude of dipole moment seems to be overestimated, its contribution was found to be less than 1 kJ $\mathrm{mol^{-1}}$ and was safely ignored. Interestingly, the sublimation enthalpy of corannulene estimated by the Williams empirical potentials agrees well with a simple empirical equation for planar PAH, $\Delta_s H°/\mathrm{kJ \cdot mol^{-1}} = 6.28n + RT$, where n is the number of carbon atoms per molecule.[13]

In Table 2 we show the comparisons among the formation enthalpies of corannulene, C_{60}, and C_{70} derived by experiment[14] and by various theoretical methods. As a general observation, *ab initio* methods with large scale basis sets, such as 6-31G*, and molecular mechanics provide better results for these nonplanar systems than do the semiempirical methods. The latter should improve in the next round of refinements, however, now that experimental data on a key nonplanar PAH have finally become available. Amazingly, the simple additivity scheme developed by Armitage and Bird[15] successfully predicts the formation enthalpy of corannulene to within 1%!

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