

Heats of Combustion of Biphenyl, Bibenzyl, Naphthalene, Anthracene and Phenanthrene

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The heats of combustion at 25°C of the following solid aromatic hydrocarbons were measured in a static-bomb calorimeter:

$$\begin{aligned}\Delta H_c^\circ (\text{biphenyl, } c) &= -1494.22 \pm 0.33 \text{ kcal mole}^{-1}, \\ \Delta H_c^\circ (\text{bibenzyl, } c) &= -1807.24 \pm 0.26 \text{ kcal mole}^{-1}, \\ \Delta H_c^\circ (\text{naphthalene, } c) &= -1232.35 \pm 0.22 \text{ kcal mole}^{-1}, \\ \Delta H_c^\circ (\text{anthracene, } c) &= -1689.17 \pm 0.41 \text{ kcal mole}^{-1}, \\ \Delta H_c^\circ (\text{phenanthrene, } c) &= -1686.06 \pm 0.30 \text{ kcal mole}^{-1}.\end{aligned}$$

These results were used to derive the heats of formation of each of the hydrocarbons. The dissociation energies of the central (C—C) bonds in biphenyl and bibenzyl were calculated to be 97.5 ± 4.5 and 56.6 ± 4.0 kcal mole⁻¹, respectively.

The heats of combustion of the aromatic hydrocarbons reported in this paper have been determined previously with discordant results, e.g., nine values of $-\Delta H_c^\circ$ have been reported for anthracene ranging from 1683.99 ± 0.20 to 1689.51 ± 0.38 kcal mole⁻¹ and it is difficult to select one value as being more reliable than the others. The calorimetry of previous investigations was probably satisfactory and it seems that the major difficulty has been in the chemical part of the investigation, i.e., in assuring the purity of the samples measured and the completeness of the combustion reaction. The samples used in this work were purified by zone-melting and the purities examined from melting-point curves. The results of the combustion experiments are based on the mass of carbon dioxide produced to minimize the effect of systematic errors due to incomplete combustion and to the presence of impurities.

It is significant that in only one previous measurement, naphthalene by Speros and Rossini,¹ was the purity of the sample established and the result based on the carbon dioxide produced. The agreement between their result and that reported below is excellent.

EXPERIMENTAL

PURIFICATION AND PURITY OF THE COMPOUNDS

Purities were measured using a thin-film melting-point apparatus based on the design described by Smit and Kateman.² The sample, *ca.* 0.5 g, was contained in the annular space between two thin aluminium cylindrical vessels (1 cm diam., 4 cm length). Temperature was measured with a platinum resistance thermometer in the inner vessel. The temperature difference between the outer vessel and an electrically heated copper shield was measured with a thermocouple and maintained constant to provide a constant rate of heat input. The fraction melted was directly proportional to time during the melting

of the sample and purities were calculated in the conventional manner by plotting temperature against the reciprocal of the fraction melted.³ The entire apparatus was surrounded by a radiation shield and placed in a large Dewar.

Anthracene was Scintillation Grade, Nuclear Enterprises, G.B. Ltd., and the other compounds were B.D.H. laboratory reagents. For each compound is given the number of times it was zone-melted and the purity expressed as mole %: biphenyl, 25, 99.99 ± 0.01; bibenzyl, 30, 99.92 ± 0.02; naphthalene, 30, 99.98 ± 0.01; phenanthrene, 72, 99.97 ± 0.01; anthracene, 99.95 ± 0.01. Although determination of purity from melting point curves is of general application, in cases where the compounds have been purified by zone refining, the possibility of erroneous results due to formation of solid solutions is increased.

CALORIMETER

The bomb calorimeter, subsidiary apparatus and technique have been described previously.⁴ The calorimeter was calibrated using thermochemical standard benzoic acid provided by the National Bureau of Standards, Washington, D.C., and by B.D.H. Ltd. The internal volume of the combustion bomb was 0.369 l. The solid hydrocarbons were burned as pellets under an initial oxygen pressure of 30 atm. The initial temperature was 25°C and an amount of substance sufficient to cause an increase of approximately 2.6°C in the temperature of the calorimeter was burned in each experiment. After each experiment the bomb gases were analyzed for carbon dioxide and the bomb washings for nitric acid. Corrections for heat losses from the calorimeter were made by the method of Coops, Jessup and van Nes.⁵

UNITS AND AUXILIARY QUANTITIES

The heats of combustion are given in joules and derived heats of formation in calories, defined by 1 cal = 4.1840 abs. J. The atomic weights used are those based on C¹² = 12.⁶ The corrections for nitric acid formation were based on 59.7 kJ mole⁻¹ for the energy of formation of 0.1 N nitric acid from N₂, O₂ and water. The energy of combustion of the cotton fuse was based on the recommended value of 16.24 kJ gm⁻¹ of cotton used. Weighings in air were corrected to vacuum using the following density values (g cm⁻³) at 20°C: biphenyl 1.180; bibenzyl 0.995; naphthalene 1.145; anthracene 1.283; phenanthrene 1.025. The carbon dioxide produced was absorbed in glass absorption tubes packed with Carbosorb. All weighings were made with oxygen in the tubes and the factor 1.00045 was used for correction to vacuum.⁷

To calculate ΔH_f° from ΔH_c° the following standard heats of formation were used: $\Delta H_f^\circ(\text{CO}_2, g) = -94.052 \text{ kcal mole}^{-1}$ and $\Delta H_f^\circ(\text{H}_2\text{O}, l) = -68.315 \text{ kcal mole}^{-1}$,⁸ where the values given in ref. (8) have been amended to comply with the atomic weights used here.

RESULTS

The results of the combustion experiments are given in tables 1-5. The symbols have the meanings:

- E_s = energy equivalent of the uncharged calorimeter system;
- E_c = energy equivalent of the contents of the bomb after combustion;
- ΔR_c = change in resistance of the platinum resistance thermometer proportional to the corrected temperature rise;
- q_i = energy of combustion of the cotton thread fuse;
- q_{nit} = energy evolved by formation of nitric acid;
- q_w = energy correction to standard states (Washburn corrections);
- $\bar{s} = \sqrt{(\bar{s}E)^2 + (\bar{s}B)^2 + (\bar{s}\Delta U_c^\circ)^2}$ = overall standard deviation of the mean value of the heat of combustion;
- $\bar{s}E$ = standard deviation of the mean value of the energy equivalent;
- $\bar{s}B$ = standard deviation of the energy of combustion of benzoic acid;
- $\bar{s}\Delta U_c^\circ$ = standard deviation of the mean value of ΔU_c° .

The number of moles of compound used in each experiment was determined from the mass of carbon dioxide produced, taking 44.00995 as the molecular weight of carbon dioxide. For each experiment is given the ratio of the mass of carbon dioxide observed to that calculated from the mass of sample. The closeness of this ratio to unity is a measure of the completeness of combustion. Tests indicated for naphthalene a loss of 0.0034 g by vaporization during the assembly of the calorimeter leading to an expected analysis ratio of 0.99966 in good agreement with the observed 0.99955. Similarly, for biphenyl an evaporation loss of 0.000064 g during assembly leads to an expected analysis ratio of 0.99993. No evaporation losses were found for the other compounds; the analysis ratio of 0.9993 for phenanthrene indicated a slight degree of incomplete combustion.

The energy equivalent E_s of the bomb calorimeter was determined from calibration experiments on the combustion of benzoic acid (under standardizing conditions, certified by N.B.S. $-\Delta u_b = 26.4338 \pm 0.0026$ kJ g⁻¹, and by B.D.H. $-\Delta u_b = 26.4390 \pm 0.0031$ kJ g⁻¹) carried out at regular intervals throughout the period of the present work. Also, recalibrations were made following any change made to the bomb itself (e.g., replacement of valves or gaskets). The final errors quoted for ΔU_c° , ΔH_c° and ΔH_f° are twice the standard deviations of the mean.

TABLE 1.—BIPHENYL

$C_{12}H_{10}$; m.w. = 154.213;

$E_s = 153.046 \pm 0.011$ kJ ohm⁻¹ (expt. 1, 2);

$E_s = 152.969 \pm 0.007$ kJ ohm⁻¹ (expt. 3);

$E_s = 152.952 \pm 0.003$ kJ ohm⁻¹ (expt. 4, 5);

$E_c = 0.197$ kJ ohm⁻¹;

$q_w = 23.7$ J.

expt.	biphenyl mmoles	CO ₂ obs./calc.	ΔR_c ohm	q_i J	q_{nit} J	$-\Delta U_c^\circ$ kJ mole ⁻¹
1	6.35949	0.99995	0.259606	40.6	1.4	6245.33
2	6.37946	0.99996	0.260445	40.6	1.3	6245.95
3	6.36068	0.99963	0.259866	41.2	2.1	6247.07
4	6.25974	0.99989	0.255621	34.2	1.8	6244.41
5	6.44461	0.99960	0.263224	38.6	1.7	6245.29
					mean value	6245.61

$\bar{s}E = 0.007$ %; $\bar{s}B = 0.005$ %; $\bar{s}\Delta U_c^\circ = 0.007$ %; $\bar{s} = 0.011$ %.

$-\Delta U_c^\circ = 1492.74 \pm 0.33$ kcal mole⁻¹; $\Delta nRT = -1.48$ kcal.

$-\Delta H_c^\circ = 1494.22 \pm 0.33$ kcal mole⁻¹.

ΔH_f° (biphenyl, c) = 24.02 ± 0.36 kcal mole⁻¹.

TABLE 2.—BIBENZYL

$C_{14}H_{14}$; m.w. = 182.268.

$E_s = 152.969 \pm 0.007$ kJ ohm⁻¹;

$E_c = 0.199$ kJ ohm⁻¹;

$q_w = 24.6$ J.

expt.	bibenzyl mmoles	CO ₂ obs./calc.	ΔR_c ohm	q_i J	q_{nit} J	$-\Delta U_c^\circ$ kJ mole ⁻¹
1	5.29332	1.00006	0.261465	40.4	3.8	7552.78
2	5.27751	0.99989	0.260669	38.5	4.1	7552.61
3	5.27904	0.99992	0.260764	39.5	3.7	7553.06
4	5.27344	0.99983	0.260487	39.7	4.3	7552.88
					mean value	7552.83

$\bar{s}E = 0.005$ %; $\bar{s}B = 0.005$ %; $\bar{s}\Delta U_c^\circ = 0.001$ %; $\bar{s} = 0.007$ %.

$-\Delta U_c^\circ = 1805.17 \pm 0.26$ kcal mole⁻¹; $\Delta nRT = -2.07$ kcal.

$-\Delta H_c^\circ = 1807.24 \pm 0.26$ kcal mole⁻¹.

ΔH_f° (bibenzyl, c) = 12.31 ± 0.31 kcal mole⁻¹.

HEATS OF COMBUSTION

TABLE 3.—NAPHTHALENE

 $C_{10}H_8$; m.w. = 128.175. $E_s = 152.969 \pm 0.007$ kJ ohm⁻¹; $E_c = 0.197$ kJ ohm⁻¹; $q_w = 25.2$ J.

expt.	naphthalene mmoles	CO ₂ obs./calc.	ΔR_c ohm	q_i J	q_{nit} J	$-\Delta U_c^\circ$ kJ mole ⁻¹
1	7.72015	0.99942	0.260096	41.4	2.4	5151.31
2	7.72937	0.99970	0.260367	41.7	2.5	5150.48
3	7.72464	0.99964	0.260254	40.8	3.3	5151.41
4	7.68045	0.99946	0.258797	41.2	5.0	5151.72
mean value =						5151.23

 $\bar{s}E = 0.005$ %; $\bar{s}B = 0.005$ %; $\bar{s}\Delta U_c^\circ = 0.005$ %; $\bar{s} = 0.009$ %. $-\Delta U_c^\circ = 1231.17 \pm 0.22$ kcal mole⁻¹; $\Delta nRT = -1.18$ kcal. $-\Delta H_c^\circ = 1232.35 \pm 0.22$ kcal mole⁻¹. ΔH_f° (naphthalene, c) = 18.57 ± 0.25 kcal mole⁻¹.

TABLE 4.—ANTHRACENE

 $C_{14}H_{10}$; m.w. = 178.236. $E_s = 152.969 \pm 0.007$ kJ ohm⁻¹; $E_c = 0.194$ kJ ohm⁻¹; $q_w = 25.0$ J.

expt.	anthracene mmoles	CO ₂ obs./calc.	ΔR_c ohm	q_i J	q_{nit} J	$-\Delta U_c^\circ$ kJ mole ⁻¹
1	5.61218	0.99987	0.259185	39.2	4.5	7061.22
2	5.64707	0.99983	0.260754	40.3	4.7	7059.92
3	5.65621	0.99998	0.261215	39.7	4.7	7061.10
4	5.65176	0.99980	0.261064	41.1	1.4	7062.91
mean value =						7061.29

 $\bar{s}E = 0.005$ %; $\bar{s}B = 0.005$ %; $\bar{s}\Delta U_c^\circ = 0.009$ %; $\bar{s} = 0.012$ %. $-\Delta U_c^\circ = 1687.69 \pm 0.41$ kcal mole⁻¹; $\Delta nRT = -1.48$ kcal. $-\Delta H_c^\circ = 1689.17 \pm 0.41$ kcal mole⁻¹. ΔH_f° (anthracene, c) = 30.87 ± 0.44 kcal mole⁻¹.

TABLE 5.—PHENANTHRENE

 $C_{14}H_{10}$; m.w. = 178.236. $E_s = 152.969 \pm 0.007$ kJ ohm⁻¹ (expt. 1, 2, 3, 4); $E_s = 152.952 \pm 0.003$ kJ ohm⁻¹ (expt. 5); $E_c = 0.194$ kJ ohm⁻¹; $q_w = 25.5$ J.

phenanthrene mmoles	CO ₂ obs./calc.	ΔR_c ohm	q_i J	q_{nit} J	$-\Delta U_c^\circ$ kJ mole ⁻¹	
1	5.66782	0.99921	0.261256	40.1	5.1	7047.52
2	5.62970	0.99947	0.259488	40.2	4.6	7047.21
3	5.65665	0.99932	0.260822	41.1	6.0	7049.35
4	5.64604	0.99940	0.260278	36.3	6.8	7048.54
5	5.67087	0.99913	0.261474	36.8	8.6	7048.79
mean value =					7048.28	

 $\bar{s}E = 0.005$ %; $\bar{s}B = 0.005$ %; $\bar{s}\Delta U_c^\circ = 0.006$ %; $\bar{s} = 0.009$ %. $-\Delta U_c^\circ = 1684.58 \pm 0.30$ kcal mole⁻¹; $\Delta nRT = -1.48$ kcal. $-\Delta H_c^\circ = 1686.06 \pm 0.30$ kcal mole⁻¹. ΔH_f° (phenanthrene, c) = 27.76 ± 0.34 kcal mole⁻¹.

TABLE 6
 $-\Delta H^\circ$, kcal mole⁻¹

	biphenyl	bibenzyl	naphthalene	anthracene	phenanthrene
Keffler, 1931 ⁹			1229.5 ± 0.3		
Beckers, 1931 ¹⁰			1230.9 ± 1.2*	1686.73 ± 0.30	
Milone and Rossignoli, 1932 ¹¹			1233.8 ± 1.5*	1689.2 ± 1.8*	1678.2 ± 1.8*
Huffman and Ellis, 1935 ¹²			1229.8 ± 0.3		
Brull, 1935 ¹³	1496.0 ± 1.5*				
Fries <i>et al.</i> , 1935 ¹⁴				1688.28 ± 0.30	1683.08 ± 0.30
Richardson and Parks, 1939 ¹⁵				1685.37 ± 0.58	1675.57 ± 0.61
Matsu and Abe, 1939 ¹⁶			1233.4 ± 0.3		
Parks <i>et al.</i> , 1946 ¹⁷		1805.65 ± 0.21		1683.99 ± 0.20	
Parks and Vaughan, 1951 ¹⁸	1493.42 ± 0.37				
Magnus <i>et al.</i> , 1951 ¹⁹				1689.51 ± 0.38	1684.64 ± 0.34
Bender and Farber, 1952 ²⁰			1229.54 ± 0.70	1687.2 ± 0.8	1685.4 ± 0.8
Coops <i>et al.</i> , 1953 ²¹		1806.78 ± 0.24		1689.0 ± 0.8	
Speros and Rossini, 1960 ¹			1232.54 ± 0.38		
Mackle and O'Hare, 1963 ²²	1493.35 ± 0.96		1230.20 ± 0.74	1686.13 ± 1.03	
this investigation	1494.22 ± 0.33	1807.24 ± 0.26	1232.35 ± 0.22	1689.17 ± 0.41	1686.06 ± 0.30

COMPARISON WITH PREVIOUS INVESTIGATIONS

The comparison is made in table 6; and, where necessary, previous results have been corrected to 25°C, to the energy units and atomic weights used here. Estimated error limits are marked *.

The only previous measurements in which the purity of the sample was examined from melting-point studies was naphthalene, by Speros and Rossini, and bibenzyl by Coops *et al.* Also Magnus *et al.* paid particular attention to the purity of the anthracene used and in these three cases the agreement with our results is within the limits of experimental error. The work of Mackle and O'Hare was done with a semi-micro bomb calorimeter and their results appear to be low suggesting that not all the difficulties inherent in this technique have been solved.

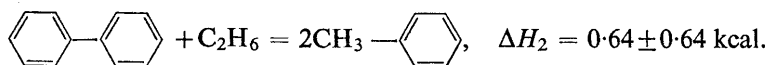
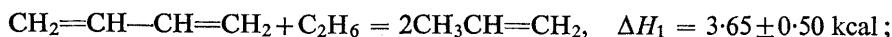
Table 6 shows that confusion can be caused by repetition of measurements unless the investigator can show that his results are more reliably established than previous ones and in this connection the purity of the sample and completeness of combustion are crucial.

DISCUSSION

To obtain heats of formation in the gaseous state, heats of sublimation are required, and that for naphthalene has been determined by Miller²³ to be 17.424 ± 0.072 kcal mole⁻¹ at 25°C. For biphenyl there are values by Bright²⁴ 17.4, Aihara²⁵ 18.1 and by Bradley and Cleasby²⁶ 19.5 ± 0.5 kcal mole⁻¹. We select the last of these in view of the fact that these authors obtained 17.3 kcal mole⁻¹ for naphthalene whereas that by Aihara was 15.8. The more recent determinations of ΔH sublimation of anthracene are by Bradley and Cleasby²⁶ 24.4; Klages²⁷ 25.0; Hoyer and Peperle²⁸ 24.3; Klochov²⁹ 24.1; Kelley and Rice³⁰ 23.45; and we select a mean value of 24.3 ± 1.0 kcal mole⁻¹. For phenanthrene there are values by Bradley and Cleasby²⁶ 20.7; Klages²⁷ 22.2; Hoyer and Peperle²⁸ 22.2; and we choose a mean value of 21.7 ± 1.0 kcal mole⁻¹. There are only two values for bibenzyl, by Bright²⁴ 17.3, and by Aihara²⁵ 20.1; we choose the latter but in view of the criticism above this value should be regarded as uncertain and further investigation is required.

kcal mole ⁻¹	$\Delta H_f(c)$	$\Delta H(sub)$	$\Delta H_f(g)$
biphenyl	24.02 ± 0.36	19.5 ± 0.5	43.52 ± 0.63
bibenzyl	12.31 ± 0.31	20.1 ± ?	32.41 ± ?
naphthalene	18.57 ± 0.25	17.42 ± 0.07	35.99 ± 0.26
anthracene	30.87 ± 0.44	24.3 ± 1.0	55.17 ± 1.1
phenanthrene	27.76 ± 0.34	21.7 ± 1.0	49.46 ± 1.1

The stabilization energy due to conjugation between the rings in biphenyl can be examined by comparing the heats of the gaseous redistribution reactions:



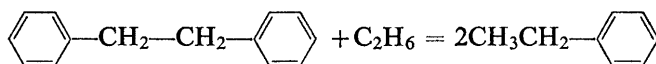
These are calculated using $\Delta H_f(\text{biphenyl}, g)$ given above; and the other ΔH_f are taken from A.P.I. tables³¹ amending the values to comply with the atomic weights used here. If we ascribe ΔH_1 to the conjugation energy (R_π) across the central C—C bond in butadiene and ΔH_2 to that across the central C—C bond in biphenyl, we conclude that this is 3 kcal less in biphenyl than in butadiene. This view has been criticized by Dewar and Schmeising³² who argue that the effects of hybridization changes of the carbon atoms on (C—C) and (C—H) bond energies should be taken into account. As shown by Skinner and Pilcher,³³ this leads to the expression for ΔH ,

$$\Delta H = R_\pi - [2E(\text{C}-\text{C}^*) - E(\text{C}-\text{C}) - E(\text{C}^*-\text{C}^*)]$$

where C represents a tetrahedral C atom and C* a trigonal C atom. If the term in brackets is the same for both reactions, then $\Delta H_1 - \Delta H_2$ still represents the difference in R_π . This reduction in R_π may be due to steric interference of hydrogen atoms causing non-planarity of the benzene rings in gaseous biphenyl.

Fielding and Pritchard³⁴ report $D(\text{Ph}-\text{H}) = 103.6 \pm 2.0$ and Duncan and Trotman-Dickenson³⁵ have given $D(\text{Ph}-\text{H}) = 102$ kcal. Taking the mean, $D(\text{Ph}-\text{H}) = 102.8 \pm 2.0$ kcal, $\Delta H_f(\text{H}\cdot, g) = 52.10 \pm 0.06$ kcal atom⁻¹,³³ $\Delta H_f(\text{benzene}, g) = 19.81 \pm 0.13$ kcal mole⁻¹,³¹ we calculate $\Delta H_f(\text{Ph}\cdot, g) = 70.5 \pm 2.0$ kcal mole⁻¹, and the dissociation energy of the central bond in biphenyl to be 97.5 ± 4.5 kcal; which is about 12 kcal mole⁻¹ greater than that for the (C—C) bond in ethane.

The heat of the gaseous redistribution reaction,



is calculated to be $\Delta H = 2.11$ kcal. According to the group additivity scheme of Benson and Buss³⁶ this reaction should be thermoneutral, and the discrepancy may be due to an incorrect ΔH sublimation of bibenzyl.

Esteban, Kerr and Trotman-Dickenson³⁷ report $D(\text{PhCH}_2-\text{H}) = 84.6 \pm 1.5$ kcal mole⁻¹. Using $\Delta H_f(\text{toluene}, g) = 11.96 \pm 0.15$ kcal mole⁻¹ we calculate $\Delta H_f(\text{PhCH}_2\cdot, g) = 44.5 \pm 1.7$ kcal mole⁻¹ and the dissociation energy of the central bond in dibenzyl to be 56.6 with an estimated uncertainty of 4.0 kcal, which is about 27 kcal mole⁻¹ less than that for the (C—C) bond in ethane.

The heat of the isomerization, anthracene(*g*) = phenanthrene(*g*) is $\Delta H = -5.71 \pm 1.5$ kcal mole⁻¹. The simple Hückel molecular orbital theory gives a difference of 0.14β between the delocalization energies.¹⁹ The observed difference is in the right direction but seems too large to be accounted by the simple theory.

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