767. *Heats of Combustion and Molecular Structure. Part VIII.* Biphenylene.*

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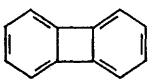
The heat of combustion of crystalline biphenylene has now been accurately measured, $-\Delta H_c^\circ = 1486{\cdot}3 \pm 0{\cdot}7$ kcal./mole, as compared with our earlier [1] approximate value of 1481 ± 5 kcal./mole. Our previous assessments [1] of molecular resonance and strain energies in this compound have been confirmed and extended.

In 1955 we reported [1] for crystalline biphenylene (then called diphenylene [2]) (I) (i) an accurate value for the latent heat of sublimation, 30·8 kcal./mole, and (ii) an approximate value for the heat of combustion, 1481 ± 5 kcal./mole. The approximate nature of the $-\Delta H_c^\circ$ value was due to its being based on only two successful combustions, owing to the scarcity of the material then available to us.



(I)

In view of the theoretical interest in the molecular structure of biphenylene, we estimated from our experimental results approximate values for the overall resonance energy, 22 ± 5 kcal./mole, of the compound and for the strain energy, 59 ± 5 kcal./mole, occasioned by the formation of the cyclobutane ring system.

As biphenylene has now become more readily accessible and as the theoretical interest in its structure has increased, it seemed desirable to obtain and to analyse an accurate value for its heat of combustion.

Experimental

Preparation of Materials.—(*a*) *Biphenylene* (J. G. C. and I. T. M.). This was prepared by pyrolysis from biphenyl-2,2′-yleneiodonium iodide as described by Baker, Boarland, and

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* Part VII, Fletcher, Mortimer, and Springall, *J.*, 1959, 580.

[1] Cass, Springall, and Quincey, *J.*, 1955, 1188.

[2] " Handbook for Chemical Society Authors," Chem. Soc., London, 1960, p. 82.

McOmie.[3] The yield depended, rather capriciously, on the cuprous oxide specimens used in the pyrolysis: aged specimens seemed to give better results. The product was purified by distillation with steam and recrystallisation from methanol, and had m. p. 110—111° (Baker *et al.*[3] give m. p. 110—111°) (Found: C, 94·2; H, 5·5. Calc. for $C_{12}H_8$: C, 94·7; H, 5·3%). The infrared absorption spectrum showed the absence of biphenyl and of hydroxylic compounds: the ultraviolet absorption spectrum was in accord with that previously reported.[4]

(*b*) *Benzoic acid.* The specimens used were " B.D.H. Thermochemical Standard."

Combustion Calorimetry.—Combustions were made in the twin-valve bomb (the Parr Instrument Co., Moline, Illinois, U.S.A.) which, together with the subsidiary apparatus, has been described previously.[5] The solid biphenylene was compressed into pellets, which were not enclosed in capsules. The vapour pressure of biphenylene is not high at 25° and the amount which volatilises after weighing and before combustion is negligible. The bomb was charged with 1 ml. of water and with oxygen at an initial pressure of 30 atm. Each sample was fired at 25°. All combustions were initiated by a platinum wire and cotton fuse, and (in experiment 1 only) an additional fuse of Melinex. After each combustion the bomb gases were analysed for carbon dioxide with an accuracy of $\pm 0{\cdot}02\%$.[6]

Units and Auxiliary Quantities.—The heats of combustion are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs. J. The energy equivalent of the calorimeter, E_s, was determined according to the method of Prosen,[7] by combustion of a sample of benzoic acid having $-\Delta U_b$ (the heat liberated in the actual bomb combustion reaction) = 6·3181 ± 0·0007 kcal./g., standard deviation, $\bar{s}B, \pm 0{\cdot}01\%$. ($E_s$ = 40061·9 cal./ohm; $\bar{s}E_s$, standard deviation, $\pm 0{\cdot}04\%$.) The heats evolved in the following ancillary processes were taken to have the values quoted: the formation of 0·1N-aqueous nitric acid from nitrogen, oxygen, and water, 13·81 kcal./mole;[7] the combustion of cotton fuse, 3·88 kcal./g.;[8] the combustion of Melinex, $(C_{10}H_4O_4)_n/n$, 1052·9 kcal./mole;[9] the combustion of carbon (soot) to carbon dioxide, 8·11 kcal./g.[8]

Results.—The results of the combustion experiments are given in Table 1, in which some of the symbols and the arrangement differ from those used in earlier Parts, to conform to recent thermochemical convention and to indicate more clearly the steps in the evaluation. Here the symbols have the following meanings: m = the weight of the sample taken (*all* weights *in vacuo*); m_i = the weight of the cotton fuse; m_m = the weight of the Melinex fuse; ΔR_c = the overall change in resistance of the platinum resistance thermometer proportional to the corrected temperature rise; m_c = the weight of unburnt carbon deposited; m_{CO_2}obs = the total weight of carbon dioxide actually produced in the combustion (from sample and fuses); m_{CO_2}calc = the total weight of carbon dioxide calculated for complete combustion of sample and fuses; CO_2obs′ : calc′ (%) = the % ratio of the weight of carbon dioxide actually produced from the sample burnt (together with the amount which would have been produced in the complete combustion of any unburnt carbon deposited) to the weight calculated for complete combustion of the sample—complete combustion of the cotton and Melinex fuses is assumed:

$$\frac{CO_2\text{obs}'}{CO_2\text{calc}'} = \frac{m_{CO_2}\text{obs} - f_i m_i - f_m m_m + f_c m_c}{m_{CO_2}\text{calc} - f_i m_i - f_m m_m}$$

where f_i = weight of CO_2/g. of cotton fuse burnt = 1·618 g., f_m = weight of CO_2/g. of Melinex fuse burnt = 2·290 g., and f_c = weight of CO_2/g. of unburnt carbon deposited = 3·667 g. m' = the total weight of the sample actually consumed in each experiment, *i.e.*, that portion completely burnt, together with that partially burnt to yield unburnt carbon: given by

$$m' = m[CO_2\text{obs}' : \text{calc}' \, (\%)/100];$$

q_i = the heat of combustion of the cotton fuse; q_m = the heat of combustion of the Melinex fuse; q_n = the heat evolved in the formation of nitric acid; q_c = the heat correction for unburnt carbon; q_w = the heat correction to standard states (Washburn correction) calculated according

[3] Baker, Boarland, and McOmie, *J.*, 1954, 1476.

[4] Heaney, Mann, and Millar, *J.*, 1957, 3930.

[5] Fletcher, Mortimer, and Springall, *J.*, 1959, 580.

[6] Prosen and Rossini, *J. Res. Nat. Bur. Stand.*, 1944, **33**, 255.

[7] Prosen, " Experimental Thermochemistry," Interscience Publ. Inc., New York, 1956, Chap. 6.

[8] Coops, Jessup, and van Nes, *op. cit.*, Chap. 3.

[9] Evans and Skinner, *Trans. Faraday Soc.*, 1959, **55**, 256.

TABLE 1.

Biphenylene (M, 152·184).

Expt.:	1	2	3	4	5
m (g.)	0·62876	0·41990	0·49673	0·58068	0·55056
m_i (g.)	0·00128	0·001365	0·001568	0·001470	0·001315
m_m (g.)	0·06998	0	0	0	0
ΔR_c (ohm)	0·16223	0·10218	0·12058	0·14084	0·13399
m_o (g.)	0	0	0	0	0
m_{CO_2} obs (g.)	2·3335	1·45495	1·71747	2·00750	1·90786
m_{CO_2} calc (g.)	2·3444	1·45932	1·72627	2·01738	1·91379
CO_2 obs′ : calc′ (%)	99·51	99·70	99·49	99·51	99·69
m' (g.)	0·62568	0·41864	0·49419	0·57783	0·54885
q_i (cal.)	5·0	5·3	6·1	5·7	5·1
q_m (cal.)	383·4	0	0	0	0
q_n (cal.)	0·5	0·6	0·4	0·6	0
q_c (cal.)	0	0	0	0	0
q_w (cal.)	3·2	2·1	2·5	3·0	2·8
E_c (cal./ohm)	6·5	4·3	4·4	4·8	4·7
$-\Delta U_c^0$ (kcal./mole)	1485·7	1485·4	1484·1	1483·8	1486·6

to Prosen;[7] E_c = the energy equivalent of the products of combustion of the sample and fuses (carbon dioxide and water) calculated from m_{CO_2}obs, m_1, and m_m by the method of Coops, Jessup, and van Nes;[8] $-\Delta U_c^\circ$ = the decrease in internal energy of the system due to the complete combustion of one mole of the substance in its standard state (crystalline biphenylene) at 25°, given by:

$$-\Delta U_c^\circ = 10^{-3}\,\frac{M}{m'}\,[(E_s + E_c)\Delta R - (q_i + q_m + q_n + q_w - q_c)]$$

The data for the derivation of the enthalpy term, $-\Delta H_c^\circ$, corresponding to $-\Delta U_c^\circ$, by the expression $-\Delta H_c^\circ = -\Delta U_c^\circ - \Delta n\boldsymbol{R}T$, where Δn is the number of moles of gas produced in the combustion reaction, are given in Table 2.

This new value for $-\Delta H_c^0$ for biphenylene coincides with the upper limit given in our earlier approximate determination.

TABLE 2.

Compound	$-\Delta U_c^\circ$ mean (kcal./mole)	Standard deviation of mean (kcal./mole)		$\Delta n\boldsymbol{R}T$ (kcal./mole)	Overall standard deviation $\bar{s}$ * (%)	$-\Delta H_c^\circ$ (kcal./mole)
		(kcal./mole)	% ($\bar{s}\Delta U_c^\circ$)			
Biphenylene ...	1485·1	±0·5	±0·03	−1·2	0·05	1486·3 ± 0·7

* Given by $\bar{s} = \sqrt{[(\bar{s}E)^2 + (\bar{s}B)^2 + (\bar{s}\Delta U_c^\circ)^2]}$ (cf. Rossini, "Experimental Thermochemistry," Interscience Publ. Inc., New York, 1956, Chap. 14).

DISCUSSION

The observed $-\Delta H_c^\circ$ term for biphenylene, 1486·3 kcal./mole, taken in conjunction with the accepted $-\Delta H_f^\circ$ terms for water and carbon dioxide, 68·32 and 94·05 kcal./mole, respectively,[10] gives standard-state heat of formation of the compound, $-\Delta H_f^\circ = -84{\cdot}4$ kcal./mole. From L_g^{st}(biphenylene) = 30·8 kcal./mole,[1] and the heats of atomisation, ΔH_a, of graphite and gaseous hydrogen at 25° (170·9 and 52·09 kcal./g.-atom, respectively)[11] we obtain the atomic heat of formation of gaseous biphenylene, $-\Delta H_{f,a} = 2352{\cdot}3$ kcal./mole.

The mean bond-energy terms, $\bar{E}$(b), used in earlier Parts for C–C, C=C, and C–H, need slight adjustment, in view of the change in the accepted value for ΔH_a(C) from 171·7 to 170·9 kcal./mole. The new $\bar{E}$(b) values are: C–C, 82·7; C=C (in *cis* C–CH=CH–C systems), 147·4; C–H, 98·65 kcal./mole (in close accord with the corresponding values currently

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[10] Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.

[11] Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publ., London, 2nd edn. 1958, p. 153.

used by Cottrell[12] and by Pauling[13]), giving $\sum\bar{E}(\text{b})$ for biphenylene = 2335·2 kcal./mole. The overall resonance stabilisation energy, E_r, of biphenylene, given by $E_r = -\Delta H_{f,a} - \sum\bar{E}(\text{b})$, is 17·1 kcal./mole. This is an exceedingly low value for a substance with two benzene ring systems in the molecule, and implies a high degree of strain associated with the four-membered ring system. This is as expected: thus, Coulson and Moffitt[14] calculated the probable order of magnitude of strain in a cyclobutadiene ring system as ~75 kcal./mole, while the recent refined re-determination of the crystal structure of biphenylene by Mak and Trotter[15] (*a*) has confirmed the predominance of the cyclobutane type structure, indicated by chemical reactivity[16] and predicted by molecular-orbital theory but not by valence-bond resonance theory[17] and (*b*) has shown that the two C–C bonds involved in both a benzene ring and the cyclobutane ring are under considerable compressional strain.

We indicated[1] that the strain could be evaluated thermochemically by comparison with biphenyl, for which substance a bond-energy term analysis of the $-\Delta H_{f,a}$ term yields a resonance energy of 81·4 kcal./mole. As the resonance energy of biphenylene is only 17·1 kcal./mole, the formation of biphenylene from biphenyl by the establishment of the cyclobutane ring system is accompanied by the establishment of a strain energy of 64·3 kcal./mole.

Another, somewhat more empirical, approach to the evaluation of this strain energy may be made by using the bond-energy terms derived by McGinn[18] for calculating, by simple summation, the heats of combustion of aromatic hydrocarbons in the gas phase at 25° (the work of Dewar and his collaborators, *e.g.*, Dewar and Schmeising,[19] provides the theoretical basis for McGinn's calculations). According to his approach there are in biphenylene eight H–C $sp^2\pi^2$ bonds (42·73 kcal./mole), six $\text{C}(sp^2\pi^2)\text{–C}(sp^2\pi^2)$ bonds (88·84 kcal./mole), four $\text{C}(sp^2\pi^2)\text{–C}(sp^2\pi^2)$ bonds (77·72 kcal./mole), and four $\text{C}(sp^2\pi^2)\text{–C}(sp^2\pi^3)$ bonds (63·93 kcal./mole). Summing these gives a theoretical "strainless" value for $-\Delta H_c{}^g$ for biphenylene of 1441·7 kcal./mole. Our experimental value is 1517·1 kcal./mole. This approach therefore gives an estimate of 75·4 kcal./mole for the strain in biphenylene.

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[12] Cottrell, *op. cit.*, p. 243.

[13] Pauling, "The Nature of the Chemical Bond," Oxford Univ. Press, London, 3rd edn., 1960, pp. 85, 189.

[14] Coulson and Moffitt, *Phil. Mag.*, 1949, **40**, 26.

[15] Mak and Trotter, *J.*, 1962, 1.

[16] Baker, McOmie, Preston, and Rogers, *J.*, 1960, 414.

[17] Longuet-Higgins, *Proc. Chem. Soc.*, 1957, 157.

[18] McGinn, *Tetrahedron*, 1962, **18**, 311.

[19] Dewar and Schmeising, *Tetrahedron*, 1960, **11**, 96, and earlier papers.