Heats of Combustion and Molecular Structure. Part III. Diphenylene.*

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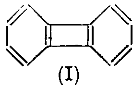
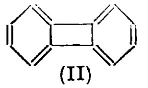
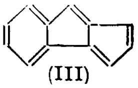
The heat of combustion and vapour pressure of diphenylene have been measured. The resonance energy of this compound has been calculated and is considered in terms of its structure.

Diphenylene was first synthesised by Lothrop (*J. Amer. Chem. Soc.*, 1941, **63**, 1187). The synthesis was confirmed by Baker (*Nature*, 1942, **150**, 210), who has also reviewed the earlier work (*J.*, 1945, 265), reported an improved synthesis, and described further reactions of this compound (Baker, Boarland, and McOmie, *J.*, 1954, 1476). The dibenzo*cyclo*butadiene structure (I) for diphenylene was advocated by Lothrop and later investigations, notably the complete *X*-ray crystal structure analysis by Waser and Chia-Si Lu (*J. Amer. Chem. Soc.*, 1944, **66**, 2035), conclusively established its correctness. It seemed desirable to investigate thermochemically the energetics of this interesting structure.


(I)


(II)


(III)

Experimental

Materials.—The benzoic acid used for the determination of the water equivalent of the calorimeter was of B.D.H. thermochemical standard grade, and the succinic acid used to check the calibration was of " AnalaR " grade. Both were stored over phosphoric oxide for several weeks before use. The diphenylene (2·9 g.), recrystallised from methanol and having m. p. 110—111°, was made available to us by Professor W. Baker, F.R.S., and was used without further purification. The density of diphenylene (1·21 ± 0·02 g./c.c.), needed for vacuum correction of weights, was determined by flotation in potassium iodide solution. Waser and Chia-Si Lu (*loc. cit.*) have reported a value of 1·24 g./c.c., using a sublimed sample.

Latent Heat of Sublimation.—The vapour pressure of diphenylene was measured over the range 98—108°, using an apparatus of the type described by Sanderson (" Vacuum Manipulation of Volatile Compounds," Wiley, New York, 1948, p. 84), the temperature being controlled to

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* Part I, *Trans. Faraday Soc.*, 1954, **50**, 815; Part II, *J.*, 1954, 2764.

within ±0·1°. For this range it was expressed by the equation $\log_{10} p_{\text{mm}} = -6755{\cdot}53/T + 18{\cdot}26$, from which the latent heat of sublimation was evaluated as 30·8 kcal./mole. The value at 25°, which could not be measured in our apparatus owing to the involatility of diphenylene at that temperature, may be assumed to be almost identical with that at the higher temperature (cf. Sidgwick, "The Covalent Link in Chemistry," Cornell Univ. Press, Ithaca, 1933, pp. 103—105).

Combustion Apparatus and Procedure.—The combustion apparatus described by Springall, White, and Cass (*Trans. Faraday Soc.*, 1954, **50**, 815) was used for this work with the following modifications. The Beckmann thermometer previously used to record the temperature rise during a combustion was replaced by a platinum resistance thermometer, the change of resistance, ΔR, being measured by means of a Smith's difference bridge (*N.P.L. Collected Researches*, 1913, **9**, 219). Temperature differences were measured with an accuracy of ±0·0002°. The temperature conditions under which the combustions were carried out differ from those described previously in that the room temperature, for this work, was controlled at 25·00° ± 0·05° and the circulating water at 28·000° ± 0·003°.

The combustion procedure followed in this work also differs slightly from that previously described. The variable value for the water equivalent of the calorimeter used in our earlier work, expressed as $E' = E + k\theta_{\text{m}}$, where θ_{m} is a "mean temperature" defined as $\theta_{10} + \Delta\theta/2$ (θ_{10} and $\Delta\theta$ being, respectively, the temperature at the time of ignition and the corrected temperature rise), is due to the variation of θ_{10}. It has been shown, as a result of thirty benzoic acid combustions, that for $\Delta\theta$ lying in the range 1·3—2·5° the water equivalent is constant, within the experimental limits of aaccuracy, provided that θ_{10} is constant. We therefore now carry out the combustions at the same firing temperature to within ±0·0002°. A 2-w heater was inserted in the calorimeter in order to reduce the time taken for the calorimeter to attain the firing temperature.

It was also found that by flushing out the bomb six times with oxygen at 10 atm. instead of twice, as in the previous work, the nitric acid correction for nitrogen-free compounds was considerably reduced.

The water equivalent (E) of the calorimeter was determined by using benzoic acid pellets, the mean value from ten combustions being 31199·0 ± 8·0 cal./ohm.

The calibration was checked by measuring the heat of combustion of succinic acid, three samples of which were burnt immediately before and three immediately after the experiments using diphenylene. The results of these two sets of combustions were identical, the value being $-\Delta U_{\text{b}} = 356{\cdot}63 \pm 0{\cdot}08$ kcal./mole. This value is in good agreement with those obtained by other workers, *viz.*, 356·68 ± 0·05 (Bechers and Roth, *Z. physikal. Chem.*, 1937, **179**, *A*, 450; and Huffman, *J. Amer. Chem. Soc.*, 1938, **60**, 1171) and 356·69 ± 0·06 kcal./mole (Pilcher and Sutton, personal communication).

The amount of diphenylene available permitted the burning of only four samples. The first two, with normal sized fuses, unfortunately failed to burn completely. The final two combustions were made cleanly by using comparatively large fuses of 0·0436 and 0·0177 g. of filter paper.

RESULTS.

The results of the last two diphenylene combustions are tabulated.

Heat of combustion of diphenylene ($M = 152{\cdot}18$).

m (vac.)	ΔR	Corrections (cals.) :			C	$-\Delta U_{\text{b}}$
(g.)	(ohms)	fuse	HNO_3	carbon	(cal./ohm)	(kcal./mole)
0·6171(7)	0·19771	173·96	0·08	1·57	4·3	1478·55
0·7477(3)	0·23591	70·62	0·21	1·58	4·3	1483·73

$$-\Delta U_{\text{b}} = M/m[(E + C)\Delta R - \text{corr.}_{\text{fuse}} - \text{corr.}_{HNO_3} + \text{corr.}_{\text{carbon}}] \times 10^{-3} \text{ kcal./mole.}$$

Mean value $-\Delta U_{\text{b}} = 1481{\cdot}1_4$ kcal./mole.
Standard deviation $(-\Delta U_{\text{b}}) = 0{\cdot}12\%$
Overall uncertainty interval $= 0{\cdot}16_5\%$
Washburn correction $(w) = 0{\cdot}95$ kcal.
$\Delta n\boldsymbol{RT} = -1{\cdot}20$ kcal.
$-\Delta H_{\text{c}}^{\circ} = 1481{\cdot}4 \pm 2{\cdot}5$ kcal./mole (from $-\Delta H_{\text{c}}^{\circ} = -\Delta U_{\text{b}} - w - \Delta n\boldsymbol{RT}$)

The value for $-\Delta H_{\text{c}}^{\circ}$, derived from only two combustion experiments, is subject to much wider limits of error than is usual. Unfortunately, no more of the valuable and rather inaccessible diphenylene can be made available. In view of the very interesting structural questions involved, we have therefore proceeded with the theoretical consideration of the problem, bearing in mind the restrictions imposed by the scantiness of the data, and using $-\Delta H_c^\circ = 1481 \pm 5$ kcal./mole.

DISCUSSION.

The dibenzo*cyclo*butadiene structure, containing a four-membered ring, must be considerably strained. Lothrop (*loc. cit.*) suggested that the Mills–Nixon effect might stabilise the molecule in the form (II). This, however, seems unlikely as the four carbon atoms which constitute the four-membered ring must be of the same trigonal planar (sp^2) type in both (I) and (II). Coulson (*Nature*, 1942, **150**, 577) reported calculations indicating that the destabilising strain energy of (I) was approximately 100 kcal./mole, whereas that of the isomeric *cyclo*pentindene (III) was only a few kcal./mole, although the total resonance stabilisation energies of both structures were nearly the same (90 and 86 kcal./mole respectively).

After the experimental establishment of structure (I) for diphenylene, the high theoretical value for the strain energy of this structure reduced. In a recalculation on *cyclo*butadiene, using the concept of "bent" bonds, Coulson and Moffitt (*Phil. Mag.*, 1949, **40**, 26) evaluated the strain energy per CH group, due to σ-bonding, as 0·8 ev. On the assumption that these results can be applied directly to the four-membered ring of diphenylene, the calculated strain energy for this compound becomes ~74 kcal./mole.

Our work was undertaken to assess experimentally the strain conditions in the established structure. This is most simply done by comparing the net molecular resonance energy, E_r, for diphenylene with that for diphenyl.

E_r for diphenylene was evaluated from our $-\Delta H_c^\circ$ and L_g^{st} values, using the method and accessory thermochemical data of Part I (*loc. cit.*). The value thus obtained for the E_r term is 22 ± 5 kcal./mole. For diphenyl, $-\Delta H_c^\circ$ is 1493·3 kcal./mole (Parks and Vaughan, *J. Amer. Chem. Soc.*, 1951, **73**, 2380). The corresponding L_g^{st} term is 17·4 kcal./mole (Bright, *J.*, 1951, 624). These values, together with the same accessory data as were used for diphenylene, yield for diphenyl, $E_r = 81{\cdot}4$ kcal./mole.

These two E_r terms indicate that the closing of the *cyclo*butadiene ring system in the transformation of diphenyl into diphenylene is accompanied by a destabilisation (strain energy) of 59 ± 5 kcal./mole. The degree of agreement between this experimental value and the value forecast in the second theoretical approach by Coulson and Moffit is encouraging.

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