33. *The Heat of Combustion of Cyclo-octadecanonaene ([18]Annulene).**

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The heat of combustion of cyclo-octadecanonaene has been measured, and the heat of formation has been calculated, $-\Delta H_f^\circ(C_{18}H_{18}, \text{cryst.}) = -39{\cdot}0 \pm 4{\cdot}0$ kcal./mole. A stabilisation energy of 100 ± 6 kcal./mole has been determined for this molecule.

THE theory of bonding in cyclic, conjugated polyenes, or annulenes, was first considered by Hückel [1] in 1931, and developed by Longuet-Higgins and Salem [2] in 1959 and by Coulson and Dixon [3] in 1962. It predicts for lower members of the series, with $(4n + 2)$ carbon atoms, a highly symmetrical structure in which all the C–C bonds are equal in length, but that for higher members of this series, *i.e.*, for large values of n, the C–C bonds will be alternately long and short. The critical value for n at which this change occurs is subject to doubt, however.

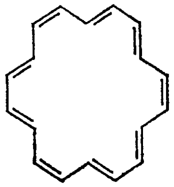
The theory also predicts that, irrespective of the value of n, all those members of the series with $4n$ carbon atoms will have alternating C–C bond lengths.

A large stabilisation energy is expected of those members which have equal C–C bond lengths, whilst for those with alternately long and short C–C bond lengths, a small stabilisation energy is expected.

Experimental thermochemical data which are available confirm that the lowest member of the series with $(4n + 2)$ carbon atoms, benzene, or [6]annulene, has a large stabilisation energy of 36 kcal./mole (based on heats of hydrogenation),[4] whilst the lowest known member of the series having $4n$ carbon atoms, cyclo-octatetraene, or [8]annulene, has a stabilisation energy of only 4·8 kcal./mole (based on heats of combustion and mean bond energy terms).[5]

Even for compounds having $(4n + 2)$ carbon atoms, in which the critical value of n is not exceeded, so that a planar molecule having bonds of equal length might be expected, steric interactions between hydrogen atoms inside the ring system may prevent the molecule adopting a planar configuration.

Mislow [6] has pointed out that [10]- and [14]-annulene, the two members of the series following benzene which have $(4n + 2)$ carbon atoms, cannot be planar because of steric interactions. Sondheimer, Wolovsky, and Amiel [7] have suggested that in [18]annulene (I) interactions are not extreme and consequently deviations of the molecule from planarity would be small.


(I)

Davies [8] has calculated a total stabilisation energy for [18]annulene, using a planar molecular model, with equal C–C bond lengths and in the absence of steric interactions, of 103 kcal./mole, on the basis of a value of 41 kcal./mole (based on heat of combustion and mean bond energy terms) for the stabilisation energy of benzene. Taking the stabilisation

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* This is Part X in the series " Heats of Combustion and Molecular Structure " (Part IX, *J.*, 1963, 3823), as well as Part XXXII in the series " Unsaturated Macrocyclic Compounds " (Part XXXI, *J. Amer. Chem. Soc.*, 1964, **86**, 521).

[1] Hückel, *Z. Phys.*, 1931, **70**, 204.

[2] Longuet-Higgins and Salem, *Proc. Roy. Soc.*, 1959, *A*, **251**, 172.

[3] Coulson and Dixon, *Tetrahedron*, 1962, **17**, 215.

[4] For a discussion of this subject see, for example, Mortimer, " Reaction Heats and Bond Strengths," Pergamon, 1962, ch. 4.

[5] Springall, White, and Cass, *Trans. Faraday Soc.*, 1954, **50**, 815.

[6] Mislow, *J. Chem. Phys.*, 1952, **20**, 1489.

[7] Sondheimer, Wolovsky, and Amiel, *J. Amer. Chem. Soc.*, 1962, **84**, 274.

[8] Davies, *Tetrahedron Letters*, 1959, **8**, 4.

energy of benzene to be 36 kcal./mole,[4] the calculated stabilisation energy of [18]annulene would be ~100 kcal./mole. Coulson and Golebiewski[9] have calculated that for a non-planar structure, in which the steric interactions are at a minimum, the loss in stabilisation energy of [18] annulene would be 70 kcal./mole.

One of the present authors (F. S.) and his co-workers have recently prepared a variety of annulenes,[10] so that it is now possible to make physical measurements on these compounds.

Longuet-Higgins and Salem[11] have interpreted the ultraviolet absorption spectrum of [18]-, [24]-, and [30]-annulene, and the proton magnetic resonance spectrum of [18]annulene to imply that the C–C bond lengths in these compounds are alternately long and short. This was also the earlier interpretation given to the ultraviolet absorption spectrum of [18]annulene by Gouterman and Wagnière.[12] More recently, however, these authors have discarded the bond-alternation hypothesis, on the basis of their low-temperature ultraviolet spectral data,[13] although they have offered no alternative explanation for the position or intensity of the ultraviolet absorption.

The refined three-dimensional *X*-ray analysis[14] of the crystal structure of [18]annulene shows that the molecule is very nearly planar, with carbon atoms displaced from the mean plane by up to 0·085 Å, and having two kinds of C–C bonds: six " outer " bonds (*cis*-configuration) of mean length 1·419 ± 0·004 Å, and twelve " inner " bonds (*trans*-configuration) of mean length 1·382 ± 0·003 Å. Although the difference, 0·04 Å, is appreciable, it is considerably less than the difference of 0·13 Å between the single and double bond lengths in cyclo-octatetraene. Moreover, the bond lengths are not alternately short and long, in that it is every third C–C bond round the ring which is a slightly longer one.

It was thought desirable to measure the heat of combustion of [18]annulene, and from this to calculate the stabilisation energy which arises from the particular C–C bonding arrangement. Measurement of the heat of combustion is here reported.

EXPERIMENTAL

Preparation of [18]*Annulene*.—The purity of the substances at all stages of the preparation was checked by thin-layer chromatography on Kieselgel G (developed with pentane–ether, and sprayed with potassium permanganate–cupric acetate reagent).

Hexa-1,5-diyne (300 g.) was oxidatively self-coupled and the product rearranged directly to give a mixture containing cyclo-octadeca-1,3,7,9,13,15-hexaene-5,11,17-triyne (tridehydro-[18]annulene), as described previously,[15] the experiments being carried out in twenty separate batches of 15 g. each. The product was chromatographed in ten equal batches, each on 3 kg. of " Alcoa " activated alumina, grade F-20 (supplied by the Aluminium Co. of America, Pittsburgh, Pa.), reactivated by heating it at 200—210° for 5 hr. It was found that the alumina as now supplied differed in properties from that obtained several years ago from the same source, giving considerably less efficient separation, being much less active than before and also giving the reversal of the order of elution of tridehydro-[18]annulene and [18]annulene described below. Even after reactivation, the efficiency of separation was inferior to that achieved previously.[15] The reason for this difference could not be ascertained from the suppliers. Ultraviolet examination of the fractions indicated that *ca.* 9·4 g. (3·2%) of tridehydro-[18]annulene had been formed. Combination of the fractions rich in the dehydro-annulene (eluted with pentane–ether, 70 : 30 to 65 : 35) yielded this substance admixed with triphenylene as well as with a yellow substance ($\lambda_{max.}$ 280 mμ). The triphenylene was removed by rechromatography in several batches on the reactivated " Alcoa " alumina (500 parts) and elution with pentane to pentane–ether (90 : 10); the column was then stripped with ether to recover the dehydro-annulene. Finally, chromatography on Florisil (500 parts; 100—200 mesh) and elution with pentane resulted in removal of the yellow impurity, the dehydro-annulene being

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[9] Coulson and Golebiewski, *Tetrahedron*, 1960, **11**, 125.
[10] Sondheimer, *Pure Appl. Chem.*, 1963, **7**, 363.
[11] Longuet-Higgins and Salem, *Proc. Roy. Soc.*, 1960, *A*, **257**, 445.
[12] Gouterman and Wagnière, *Tetrahedron Letters*, 1960, No. 11, 22.
[13] Gouterman and Wagnière, *J. Chem. Phys.*, 1962, **36**, 1188.
[14] Bregman, Hirshfeld, Rabinovich, and Schmidt, private communication.
[15] Sondheimer and Wolovsky, *J. Amer. Chem. Soc.*, 1962, **84**, 260.

eluted first. Crystallisation from pentane then yielded pure tridehydro-[18]annulene (6·1 g.; 2·1%), homogeneous by thin-layer chromatography, and exhibiting the reported physical properties.[15]

The partial hydrogenation of tridehydro-[18]annulene (4·2 g.) was carried out as described before,[7] in batches of 300—400 mg. each. The yield of [18]annulene, determined spectroscopically, varied between 18 and 25%. Chromatography of a sample on the above-mentioned " Alcoa " alumina resulted in very poor separation, and in elution of [18]annulene before unchanged tridehydro-[18]annulene (a reversal of the order observed previously [7]). On the other hand, chromatography of a sample on " Merck " acid-washed or " Woelm " alumina resulted in the usual sequence, and also gave satisfactory separation. The bulk of the material was therefore chromatographed in several batches on the " Merck " alumina (500 parts). Crystallization then yielded pure [18]annulene (640 mg.; 15%), homogeneous by thin-layer chromatography, and showing the reported physical properties.[7] A solution of this material (495 mg.) in tetrahydrofuran (*ca.* 50 ml.; redistilled over sodium) was sealed in a glass tube under nitrogen, and sent by air-mail from Rehovoth to Keele.

On arrival in Keele, the tetrahydrofuran solution, containing [18]annulene and polymeric material formed in transit, was put on to a column of neutral activated alumina, type " O " (Peter Spence and Sons Ltd., Widnes). The system was then eluted with pentane which first removed the tetrahydrofuran and then the annulene, leaving the polymer (*ca.* 200 mg.) on the column. The pentane solution of annulene was evaporated at reduced pressure at a temperature not exceeding 40°. The crystalline [18]annulene was dried at room temperature/10—20 mm. pressure for 2 hr. Purification was carried out immediately before the combustions, which were completed within a period of 12 hr. since the compound is considerably less stable as solid than in solution.[7]

Combustion Calorimetry.—Combustions were made in a twin-valve bomb (the Parr Instrument Co., Moline, Illinois, U.S.A.) which, together with the subsidiary apparatus, has been described previously.[16] The solid compound was compressed into pellets which were sealed in Melinex bags. In one experiment, in which no bag was used, the compound ignited spontaneously whilst the bomb was being charged with oxygen under pressure. [The compound did not appear to be perceptibly oxidised by air, at atmospheric pressure, since the weight of a pellet remained unchanged in air over a period of 30 min., and also, after combustion, the recovery of carbon dioxide from a pellet, handled in this way, was as high as 99·88% of the theoretical quantity (see below).] 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. After each combustion the bomb gases were analysed for carbon dioxide to an accuracy of $\pm 0{\cdot}02\%$.[17] The energy equivalent of the calorimeter, E_s, was determined according to Prosen's method,[18] by combustion of a sample of benzoic acid (B.D.H. Thermochemical Standard, batch no. 76016) having $-\Delta U_b = 6319{\cdot}1 \pm 0{\cdot}7$ kcal./g., standard deviation, $\bar{s}B$, $\pm 0{\cdot}011\%$. ($E_s = 41560{\cdot}6$ cal./ohm; sE, $\pm 12{\cdot}5$ cal./ohm, standard deviation $\pm 0{\cdot}03\%$.)

The heats evolved in the following ancillary processes were taken to have the value quoted: the combustion of cotton fuse, 3·88 kcal./g.; [18] the formation of 0·1N-aqueous nitric acid from nitrogen, oxygen, and water, 13·81 kcal./mole; [19] and the combustion of carbon (soot) to carbon dioxide, 8·11 kcal./g.[18] The heat of combustion ($-\Delta U_c$) of Melinex ($C_{10}H_8O_4$), which had been dried over phosphorus pentoxide before combustion, was found to be $5{\cdot}4833 \pm 0{\cdot}0005$ kcal./g., based on the weight (uncorrected to *vacuo*) of sample taken. Only 99·73% of the theoretical amount of carbon dioxide, corresponding to the formula $C_{10}H_8O_4$, was recovered after combustion.

Units.—The heats of combustion are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs.J. Atomic weights used are those recommended by the International Union in 1961,[20] and heats of formation quoted from other sources have been recalculated in terms of these atomic weights. All weights used were calibrated against N.P.L. standards.

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

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

[18] Coopes, Jessup, and van Nes, " Experimental Thermochemistry," Vol. 1, ed. Rossini, Interscience, New York, 1956, ch. 3.

[19] Prosen, " Experimental Thermochemistry," Vol. 1, ed. Rossini, Interscience, New York, 1956, ch. 6.

[20] *J.*, 1961, 5564.

Results.—The results of the combustion experiments are given in the Table. The method of calculation and meanings of symbols are the same as those given in Part VIII [21] except that here f_m = 2·28352 g. of CO_2/g. of Melinex. The corrections E_c and q_w refer to the mixture of Melinex and [18]annulene.

The value of $-\Delta H_c^0$ for [18]annulene refers to the reaction

$$C_{18}H_{18}(cryst.) + 22{\cdot}5\ O_2(g) \longrightarrow 18\ CO_2(g) + 9\ H_2O(liq.)$$

Shortage of sample allowed only three successful combustions to be carried out. Low recovery of carbon dioxide after the last experiment resulted, most probably, from the presence of a trace of alumina in the solid sample, introduced during the purification procedure, rather than from incomplete combustion of the sample. Because of these difficulties, the magnitude of the probable limits of error, ±4·0 kcal./mole in ΔH_c^0 is greater than is usual, but in view of the very interesting structural questions involved we have proceeded with the theoretical consideration of the problem, bearing in mind the rather wide limits of error.

[18]Annulene (*M*, 234·34).

Expt.:	1	2	3
m (g.) *	0·063110	0·075665	0·0417300
m_i (g.)	0·003358	0·003415	0·003602
m_m (g.)	0·101329	0·216305	0·205610
ΔR_c (ohm)	0·02870	0·04681	0·03696
m_c (g.)	0·000740	—	—
m_{CO_2} (obs.) (g.)	0·48195	0·75135	0·60889
m_{CO_2} (calc.) (g.)	0·48465	0·75670	0·61779
CO_2 (obs′ : calc′) (%)	99·88	98·48	94·67
m' (g.)	0·063031	0·745149	0·395045
q_i (calc.)	13·03	13·25	13·98
q_m (cal.)	555·67	1186·18	1127·53
q_n (cal.)	0·55	0·14	0·21
q_c (cal.)	6·00	—	—
q_w (calc.)	0·29	0·35	0·12
E_c (cal./ohm)	2·21	2·26	2·22
$-\Delta U_c^\circ$ (kcal./mole)	2341·8	2348·0	2342·5

The $-\Delta U_c^\circ$ terms are given by the expression $-\Delta U_c^\circ = 10^{-3}\frac{M}{m'}[(E_s + E_c)\Delta R - (q_i + q_m + q_n + q_w - q_c)]$.

Mean $-\Delta U_c^\circ = 2344{\cdot}1 \pm 4{\cdot}0$ kcal./mole
$-\Delta H_c^\circ = -\Delta U_c^\circ - \Delta n\boldsymbol{R}T$
$\Delta n\boldsymbol{R}T = -2{\cdot}68$ kcal./mole
$-\Delta H_c^\circ = 2346{\cdot}8 \pm 4{\cdot}0$ kcal./mole.

* Weights *in vacuo*, d_{25} = 4·42 g./ml.

DISCUSSION

The observed $-\Delta H_c^\circ$ term for [18]annulene, 2346·8 ± 4·0 kcal./mole, taken in conjunction with the accepted $-\Delta H_f^\circ$ terms for liquid water and gaseous carbon dioxide, 68·315 ± 0·010 and 94·052 ± 0·011 kcal./mole,[22] respectively, gives the standard-state heat of formation of the compound, $-\Delta H_f^\circ$ (cryst.) = −39·0 ± 4·0 kcal./mole. The latent heat of sublimation of this compound has not been measured, but for the compounds naphthacene, triphenylene, and chrysene, of molecular formula $C_{18}H_{12}$, the latent heats of sublimation lie in the range 26—30 kcal./mole.[23] If the latent heat of [18]annulene is taken to have the value 28 ± 2 kcal./mole, then we have $-\Delta H_f^\circ$ (g) = −67 ± 6·0 kcal./mole.

The heat of formation of gaseous benzene being taken as $-\Delta H_f^\circ$(g) = −19·82 kcal./mole,[24] the heat of the hypothetical isomerisation reaction

$$3C_6H_6(g) \longrightarrow C_{18}H_{18}(g)$$

may be calculated as ΔH = +8·0 ± 6·0 kcal./mole. If this were a thermoneutral reaction

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[21] Bedford, Carey, Millar, Mortimer, and Springall, *J.*, 1962, 3895.
[22] Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.
[23] Magnus, Hartman, and Becker, *Z. phys. Chem.*, 1951, **197**, 75.
[24] American Petroleum Institute Research Project 44, Carnegie Press, Pitt., Pa., 1953.

then the stabilisation energy of [18]annulene would be three times that of benzene,[4] $(3 \times 36) = 108$ kcal./mole. The positive value of ΔH indicates that the stabilisation energy is less than 108 kcal./mole by the value of ΔH, viz. 100 ± 6 kcal./mole.

Although the limits of error are comparatively large, the measured heat of formation of [18]annulene is sufficiently accurate to show that the stabilisation energy is close to that calculated by Davies.[8] The thermochemical results are, therefore, in general agreement with the *X*-ray structural analysis: the molecule is nearly planar and is not seriously deformed, since such deformation would result in a very much smaller value for the stabilisation energy of the molecule.

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