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Note

The standard enthalpies of formation of some dibenzocycloheptane ketones

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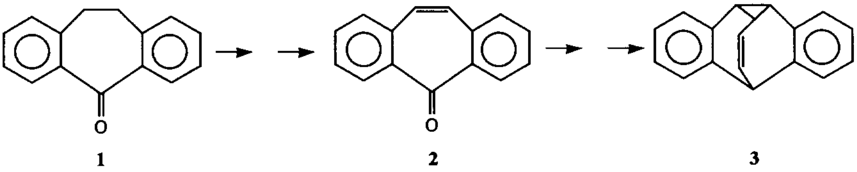
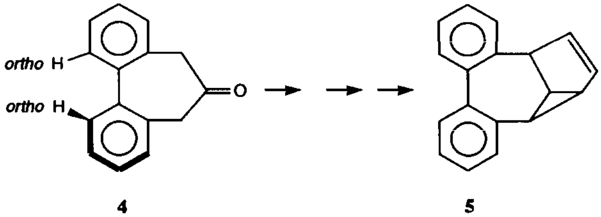
Abstract

The heats of combustion of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]-cycloheptene-5-one (ketone **1**), 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (ketone **2**) and 5,7-dihydro-6*H*-dibenzo[*a*,*c*]cyclohepten-6-one (ketone **4**) were measured by means of a Gallenkamp adiabatic bomb calorimeter. Uncertainties in the determination of the heats of combustion ranged between 0.25% and 2%. The enthalpies of formation and of atomization for the three compounds were derived. The experimental values of the heats of atomization in the solid state were compared with those calculated using the Allen–Skinner bond energy scheme (for the liquid state). Conclusions concerning the resonance energies of the three compounds are drawn.

INTRODUCTION

The valence isomers of annulenes, as well as of their benzo-annelated derivatives, have been studied intensively [1]. However very few thermodynamic data are available for these compounds.





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In previous papers, the syntheses of some dibenzo-annelated valence isomers of [10] annulene, e.g. **3** and **5** were described [2,3]. The corresponding multi-step syntheses of **3** and **5** involved the intermediate formation of the dibenzocycloheptane ketones **1**, **2** and **4**.

In this paper the enthalpies of formation of ketones **1**, **2** and **4**, obtained from their heats of combustion, are presented.

EXPERIMENTAL

Ketone **1** (10,11-dihydro-5*H*-dibenzo[*a*, *d*]cyclohepten-5-one) was prepared following the procedures of Cope and Fenton [4] and of Campbel [5]; it was then purified by distillation (boiling point, 133–134°C).

Ketone **2** (5*H*-dibenzo[*a*, *d*]cyclohepten-5-one) was obtained by the method of Cope and Fenton [4], and was purified by recrystallization from ethanol (melting point, 89°C).

Ketone **4** (5,7-dihydro-6*H*-dibenzo[*a*,*c*]cyclohepten-6-one) was synthesized after the method of Eistert and Minas [6], and purified by recrystallization from ethanol (melting point, 78°C).

A Gallenkamp CB-110 adiabatic bomb calorimeter was used. The oxygen was of $\geq$99% purity. The combustion experiments were performed as described previously [7].

RESULTS AND DISCUSSION

The obtained calorimetric results for combustion of ketones **1**, **2** and **4** are presented in Tables 1–3. The mean values for the enthalpies of formation and atomization are shown in Table 4.

TABLE 1

Data from the combustion experiments of ketone **1**

m(pellet)/g [a]	0.95455	1.02665	1.07750	0.89365	1.10413
ΔT/K [b]	3.155	3.390	3.562	2.951	3.647
q(cotton)/J [c]	106.1	55.3	106.1	74.3	106.1
q(Cr–Ni)/J [c]	4.1	2.8	3.4	3.5	3.0
$q(HNO_3)$/J [c]	25.1	25.1	25.1	25.1	3.8
$-\Delta u_c^{\ominus}/(\mathrm{J\,g^{-1}})$ [d]	35960.7	35986.2	35979.7	35954.1	35945.8
$-\Delta U_c^{\ominus}/(\mathrm{kJ\,mol^{-1}})$ [d]	7488.8	7494.1	7493.6	7487.4	7485.7
$-\Delta H_c^{\ominus}/(\mathrm{kJ\,mol^{-1}})$ [e]	7495.0	7500.3	7499.8	7493.2	7491.9
$-\Delta H_f^{\ominus}/(\mathrm{kJ\,mol^{-1}})$ [f]	124.7	119.2	119.7	126.1	127.9
$\Delta H^{\ominus}/(\mathrm{kJ\,mol^{-1}})$ [g]	13718.9	13713.6	13714.1	13720.4	13722.2

[a] Sample mass. [b] Temperature rise of the bomb calorimeter. [c] Heats due to ignition and formation of nitric acid. [d] Standard energy of combustion. [e] Standard enthalpy of combustion. [f] Standard enthalpy of formation. [g] Enthalpy of atomization.

TABLE 2

Data from the combustion experiments of ketone **2**[a]

m(pellet)/g	0.93600	0.96114	0.95550	0.89940	0.98515	0.93830
ΔT/K	3.067	3.134	3.130	2.931	3.202	3.050
q(cotton)/J	79.6	79.6	79.6	106.1	106.1	106.1
q(Cr–Ni)/J	0.0	0.0	4.3	5.4	5.9	3.6
$q(\mathrm{HNO_3})$/J	25.1	25.1	25.1	25.1	24.3	25.5
$-\Delta u_c^{\ominus}/(\mathrm{J\,g^{-1}})$	35679.1	35506.9	35666.7	35443.9	35363.0	35361.9
$-\Delta U_c^{\ominus}/(\mathrm{kJ\,mol^{-1}})$	7358.1	7322.6	7355.6	7309.6	7292.9	7292.7
$-\Delta H_c^{\ominus}/(\mathrm{kJ\,mol^{-1}})$	7363.0	7323.7	7360.5	7314.5	7297.8	7297.6
$\Delta H_f^{\ominus}/(\mathrm{kJ\,mol^{-1}})$	29.5	−6.1	26.9	−19.0	−35.7	−36.0
$\Delta H^a/(\mathrm{kJ\,mol^{-1}})$	13128.4	13164.0	13131.0	13176.9	13193.6	13193.9

[a] For key, see Table 1 footnotes.

TABLE 3

Data from the combustion experiments of ketone **4**[a]

m(pellet)/g	0.95120	0.97582	0.91080	0.93005
ΔT/K	3.172	3.260	3.050	3.112
q(cotton)/J	104.7	107.3	79.6	79.6
q(Cr–Ni)/J	0.0	3.4	2.6	3.7
$q(\mathrm{HNO_3})$/J	25.1	25.1	25.1	25.1
$-\Delta u_c^{\ominus}/(\mathrm{J\,g^{-1}})$	36285.7	36351.3	36462.4	36420.5
$-\Delta U_c^{\ominus}/(\mathrm{kJ\,mol^{-1}})$	7556.5	7570.2	7593.3	7584.6
$-\Delta H_c^{\ominus}/(\mathrm{kJ\,mol^{-1}})$	7562.7	7576.4	7599.5	7590.7
$-\Delta H_f^{\ominus}/(\mathrm{kJ\,mol^{-1}})$	56.9	43.2	20.0	28.8
$\Delta H^a/(\mathrm{kJ\,mol^{-1}})$	13650.8	13637.1	13614.0	13622.8

[a] For key, see Table 1 footnotes.

TABLE 4

Enthalpies of formation $\Delta H_f^{\ominus}$ and enthalpies of atomization ΔH^a for ketones **1**, **2** and **4**

Ketone	$\Delta H_f^{\ominus}(\mathrm{s})/(\mathrm{kJ\,mol^{-1}})$	$\Delta H^a_{\mathrm{exp}}(\mathrm{s})/(\mathrm{kJ\,mol^{-1}})$	$\Delta H^a_{\mathrm{calc}}(\mathrm{l})/(\mathrm{kJ\,mol^{-1}})$
1	−123.5 ± 3.4	13717.8 ± 3.4	13647.7
2	−6.7 ± 26.7	13164.6 ± 26.7	13073.9
4	−37.2 ± 14.0	13631.1 ± 14.0	13651.9

The uncertainties in the enthalpies of formation for the three ketones are different: 0.25% for **1**, and 2% for **2**, from the corresponding heats of combustion. These differences may be attributable to the different purities of the corresponding products.

The last column of Table 4 gives the enthalpies of atomization in the liquid state, calculated by means of the Allen–Skinner bond energy scheme. The required parameters for these calculations can be found in refs. 7 and 8. It can be observed that for ketone **1** the difference between the two enthalpies of atomization is higher than the normal value of the heat of melting for compounds of this type (20–45 kJ mol^{-1}). Thus, a resonance energy (E_r) of at least 30 kJ mol^{-1} seems to stabilize this structure (without taking into account the E_r value of the benzenoid rings).

Following a similar argument, a resonance energy of more than 50 kJ mol^{-1} can be deduced for ketone **2** (again without considering the benzenoid rings E_r). This value can be attributed to the conjugated tropone moiety included in this molecule.

In the case of ketone **4**, the difference between the two enthalpies of atomization equals the heat of melting (within the limits of the uncertainties). It seems that the geometry of ketone **4** imposes a non-coplanarity on the two aromatic rings, thus diminishing their conjugation. In fact, a steric hindrance between the two orthohydrogens in ketone **4** is easily observable on Dreiding stereomodels. Moreover, in ketone **4** the carbonyl group is unconjugated with the benzenoid rings, whereas in both ketones **1** and **2** a conjugation between the carbonyl group and the two β-situated phenyl rings is possible.

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