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The standard enthalpies of formation of some dibenzoannelated cycloalkanols

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Abstract

The heats of combustion of *trans*-9,10-bis-hydroxymethyl-9,10-dihydrophenanthrene, *trans*-5-hydroxymethyl-5,6-dihydro-7H-dibenzo[*a,c*]cyclohepten-6-ol, 5-hydroxymethyl-5,6-dihydro-7H-di-benzo[*a,c*]cycloheptene, 6-hydroxymethyl-5,6-dihydro-7H-dibenzo[*a,c*]cycloheptene, 5H-dibenzo-[*a,d*]cyclohepten-5-ol and 5H-10,11-dihydrodibenzo[*a,d*]cyclohepten-5-ol were measured by means of a Gallenkamp adiabatic bomb calorimeter. Uncertainties in the determination of the heats of combustion ranged between 0.2 and 0.3%. The enthalpies of formation and atomization for the six compounds were derived. The experimental values of the heats of atomization were compared with those calculated using the Allen–Skinner bond energy scheme. Conclusions about energetic contributions which stabilize the structure of the investigated compounds were drawn. © 1998 Elsevier Science B.V.

Keywords: Allen–Skinner bond energy scheme; Combustion calorimetry; Dibenzoannelated cycloalcanols; Enthalpy of formation

1. Introduction

This paper continues our thermochemical investigation of some dibenzoannelated seven membered ring compounds [1]. The study started with some ketones of this type. Few thermodynamic data seem to be available for dibenzoannelated cycloalkanols (in contrast with numerous researches devoted to non-annelated cyclic alcohols). During our investigations of carbocationic rearrangements of dibenzocycloalkane systems [2], we described the first syntheses of diols 3, 5 and of the alcohol 8 using reaction sequences outlined in Scheme 1 [3].

Intending to study comparatively the enthalpies of formation of some related dibenzoannelated cycloalkanols, we added to the above mentioned compounds 3, 5, 8 the known alcohols 9 [4], 10 [5] and 11 [6] (see Scheme 2).

In this way two sets of isomeric alcohols, namely 3 and 5 ($C_{16}H_{16}O_2$) and 8 and 9 ($C_{16}H_{16}O$), along with a set of unsaturated (10)/saturated (11) dibenzocycloheptanols were constituted, allowing an efficient comparison.

2. Experimental

Diols 3, 5 and the alcohol 8 were synthesized as described in our previous paper [3], following the reaction sequences indicated in Scheme 1. The

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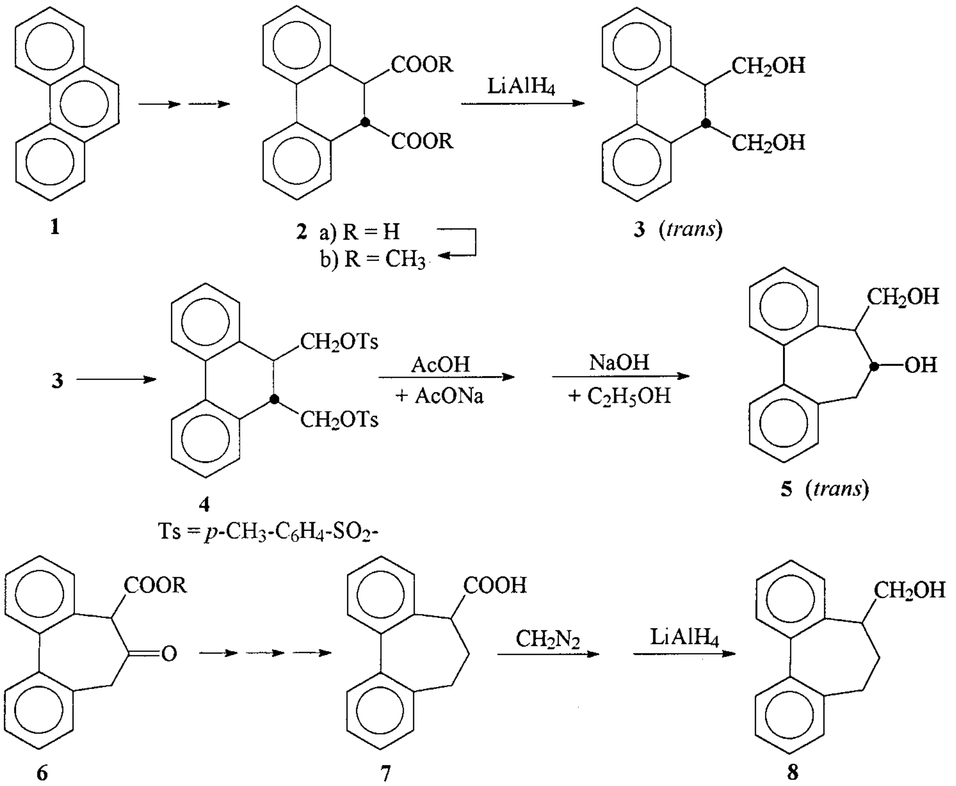
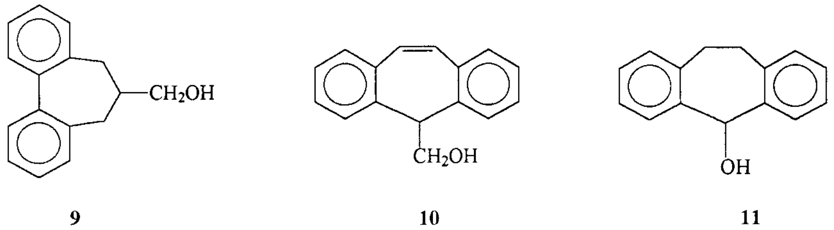


Scheme 1.



Scheme 2.

trans-diol 3 (*trans*-9,10-bis-hydroxymethyl-9,10-dihydrophenanthrene) – m.p. 177–178°C – was recrystallized twice from ethanol.

The *trans*-diol 5 (*trans*-5-hydroxymethyl-5,6-dihydro-7H-dibenzo[*a,c*]cyclohepten-6-ol) – m.p. 123°C – was recrystallized twice from benzene.

The alcohol 8 (5-hydroxymethyl-5,6-dihydro-7H-dibenzo[*a,c*]cycloheptene) – m.p. 79°C – was recrystallized twice from *n*-hexane.

Alcohol 9 (6-hydroxymethyl-5,6-dihydro-7H-dibenzo[*a,c*]cycloheptene) – m.p. 133–135°C – was synthesized following the procedure of Beaven et al. [4] and purified by double recrystallization from benzene/petroleum ether.

The compound 10 (5H-dibenzo[*a,d*]cyclohepten-5-ol) – m.p. 123–124°C – was synthesized according to the method of Berti [5]. It was purified by double recrystallization from benzene.

Alcohol 11 (5H-10,11-dihydrodibenzo[*a,d*]cyclohepten-5-ol) – m.p. 93°C – was synthesized following the method of Mychailyszin and Protiva [6] and purified by recrystallization from *n*-hexane–diethylether mixture.

In combustion experiments, a Gallenkamp CB-110 adiabatic bomb calorimeter was used. The combustion experiments, using oxygen of over 99% purity were performed as described previously [1,7]. The calorimeter was calibrated by means of the combustion of calorimetric standard benzoic acid ($\Delta_c u^0 = -26433.8$ J/g). We found an energy equivalent of the calorimeter of 10857±7 J/K. All weight measurements were done with an analytical balance with an accuracy of $\pm 1\times 10^{-5}$ g. The mercury thermometer of the calorimeter was accurate within $\pm 2\times 10^{-3}$ K. The samples were fired by means of a weighed cotton fuse ($\Delta_c u = 7324.0$ J g^{-1}). The bomb was flushed and filled with oxygen at ca. 30 bar. Runs were rejected when there was any visible evidence of soot in the bomb, or in the crucible. The reduction of data to the standard state was done by following the procedure recommended in the book of Rossini [8].

3. Results and discussion

An example of data concerning the combustion experiments for one of the six investigated alcohols is presented in Table 1. Four-to-six experiments were done for each compound, depending on the available amount of substance (the syntheses are difficult and proceed with poor yields). In Table 2, the mean values of the enthalpies of formation and atomization in the solid state are summarized together with the enthalpies of atomization of the compounds in the liquid state, calculated by means of the Allen–Skinner bond energy scheme [9]. The required parameters for $\Delta_a H_{calc}(l)$ were taken from Refs. [7,9–11].

Table 2
Enthalpies of formation $\Delta_f H^0$ and enthalpies of atomization $\Delta_a H$ for the six alcohols

Compound	ΔH_f^0(s)/ (kJ mol^{-1})	ΔH^a_{exp}(s)/ (kJ mol^{-1})	ΔH^a_{calc}(s)/ (kJmol^{-1})
3	−415±14	15845	15764
5	−423±17	15854	15773
8	−219±14	15400	15327
9	−221±14	15402	15328
10	−107±19	13701	13604
11	−205±19	14235	14143

The experimental enthalpies of atomization of the solid compounds were calculated with the equation:

$$\Delta_a H_{exp}(s) = \sum \Delta_f H^0(\text{atoms, ideal gas}) - \Delta_f H^0(\text{compound, solid})$$

For compound 3, e.g. $\Delta_a H_{exp}(s)$ is associated to the reaction:

$$C_{16}H_{16}O_2(s) \rightarrow 16C(g) + 16H(g) + 2O(g)$$

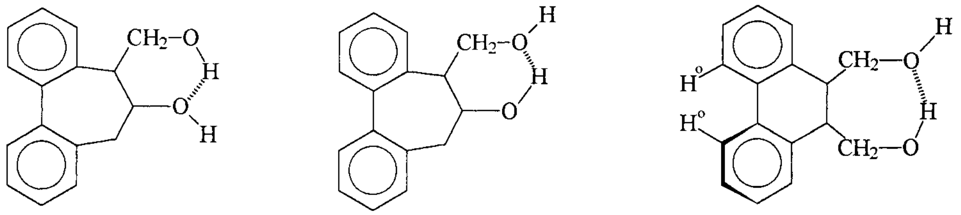
The uncertainties in the determination of the heats of combustion ranged between 0.2–0.3%.

The discussion of the results reported in Table 2 is done by comparing the experimental and calculated values of the heats of atomization. Values of the heats

Table 1
Data from the combustion experiments of alcohol 8

m (pellet)/g	0.88700	0.88800	0.82500	0.90000	0.93565
ΔT/K [a]	3.050	3.051	2.850	3.100	3.229
q (cotton)/J [b]	117.6	100.7	134.2	85.9	142.3
q (HNO_3)/J [b]	27.0	27.4	28.0	25.1	25.1
q (Cr-Ni)/J [b]	5.1	3.4	4.0	5.1	1.9
$-\Delta_c u^0$/(Jg^{-1}) [c]	37189	37179	37329	37292	37312
$-\Delta_c U^0$/(kJ mol^{-1}) [c]	8341.5	8339.4	8373.0	8364.8	8369.3
$-\Delta_c H^0$/(kJ mol^{-1}) [d]	8350.2	8348.1	8381.7	8373.5	8378.0
$-\Delta_f H^0$/(kJ mol^{-1}) [e]	234.8	236.9	203.3	211.4	206.9

[a] Temperature rise in the bomb calorimeter.
[b] Heats due to ignition and formation of nitric acid.
[c] Standard energies of combustion.
[d] Standard enthalpy of combustion.
[e] Standard enthalpy of formation.



5A **5B** **3**

Scheme 3.

of melting of the investigated compounds of 30–50 kJ/mol were considered.

The structure of diol 3 presents a stabilization energy (without consideration of the resonance energies of benzenoid rings, which are included in the bond energies) of >30 kJ/mol. About two thirds of this value are probably due to the formation of internal hydrogen bonds, between the hydroxyl groups; the rest corresponds to the conjugation between the benzenoid rings, which are almost co-planar in this compound (dihedral angle 10–15°).

The stabilization energy of compound 5 exceeds by 5–10 kJ/mol that of compound 3 because of the formation of an additional stable six-membered ring including a hydrogen bond (see Scheme 3). The seven-membered ring containing the same type of hydrogen bond of diol 3 implies a higher strain, as well as the more close ortho-hydrogens of the benzenoid rings.

A resonance energy of at least 20 kJ/mol is present in alcohols 8 and 9, despite the non-coplanarity of the benzenoid rings. Their enthalpies of formation and atomization have very close values, as expected according to the additivity schemes.

The heat of hydrogenation of alcohol 10 to alcohol 11, calculated by means of the corresponding experimental enthalpies of formation, has a normal value of ca. 100 kJ/mol characteristic to a carbon=carbon double bond with such substituents. An estimated value of 50–70 kJ/mol is obtained for the resonance energy of compound 10, while for 11 the same value should be at least 40 kJ/mol. These values of resonance energies are in qualitative agreement with those of the corresponding ketones, reported in Ref. [1].

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