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Research paper

The determination of resonance energy in conjugated benzenoids: A combined experimental and theoretical approach

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A R T I C L E I N F O

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A B S T R A C T

The conjugated circuits model of aromaticity in benzenoids is reconsidered. Values for the parameters R_1, R_2, and R_3 are rederived from experimental enthalpies of formation. It is shown that the value of R_3 depends on the shape as well as the size of a 14-cycle. R_3 values are found to obey the relation $R_3^{pyrene} > R_3^{anthracene} > R_3^{phenanthrene}$.

1. Introduction

The concept of resonance energy—the extra energetic stability of molecules in which electrons can partially delocalize from classical chemical bonds—has an enormous history in chemistry, with literally thousands of scientific papers addressing the subject. In this paper the aromatic resonance energy of benzenoid hydrocarbons is considered, based in so far as possible on experimentally measured heats of formation, but supplemented by theoretical calculations when necessary. By benzenoid hydrocarbons is meant molecules such as benzene and naphthalene composed solely of carbon and hydrogen atoms with the carbon atoms arranged in six-membered rings which support more than one Kekule structure. Aromatic resonance energy therefore arises from delocalization of the pi electrons of the carbon-carbon double bonds due to interactions between Kekule structures.

One of the most successful approaches to resonance energy is the conjugated circuits model originally introduced by Herndon [1] and extended by Randic [2]. A conjugated n-circuit is simply a set of alternating double and single bonds extending around the perimeter of an n-membered ring of carbon atoms. Herndon considered only 6- and 10-circuits in his original work but Randic extended the idea by adding 14-circuits. He parameterized his theory by choosing values for the contributions of 6-, 10-, and 14-circuits to reproduce Dewar and De Llano's [3] calculated semiempirical resonance energies for benzene, naphthalene, and anthracene. This theory has been extended to include rings of other than six carbon atoms as well as heteroatoms [4–7].

In this work the values for the parameters for 6-, 10-, and 14-cicuits, which following Randic will be denoted as R_1, R_2, and R_3, will be rederived using experimental heats of formation in place of semiempirical calculations. The interest in doing this comes from a suggestion by Klein and Trinajstic [8] that the value for R_3 should depend on the shape as well as the size of the circuit. A shown in Figs. 1–3, 14-circuits can extend around the perimeter in some of the Kekule structures of anthracene, phenanthrene, or pyrene. Based on low-order resonance theory, Klein and Trinajstic predicted

$$R_3^{pyr} = 7/3R_3^{anth} = 14/3R_3^{phen} \qquad (1)$$

though the precise value of the coefficients will change somewhat at higher orders.

There is some evidence for this from Randic's original work. He obtained $R_3 = -9.6$ kJ/mol (converted from electron volts using the conversion 1 eV = 96.4853 kJ/mol). But if he had used Dewar and De Llano's value for phenanthrene he would have obtained $R_3 = +0.5$ kJ/mol while if he had used pyrene he would have gotten $R_3 = -3.1$ kJ/mol.

The experimental enthalpies of formation used in this paper are summarized in Table 1. Except for phenanthrene, all are from the most recent Handbook of Chemistry and Physics [9] with uncertainties from [10]. The value for phenanthrene is from a more recent measurement by Nagano [11] which corrects a significant error of 6 kJ/mol in the previously accepted literature value.

By far the most important contribution to the energy of a molecule relative to separated atoms is simply the energy of the localized bonds. But in benzenoid aromatics the number of C—C, C=C, and C—H bonds is linearly dependent. Therefore in this work only isodesmic chemical reactions (reactions with the same number of each type of bond in the same environment) will be used, so that bond energies will cancel out. This allows a direct focus on the aromaticity.

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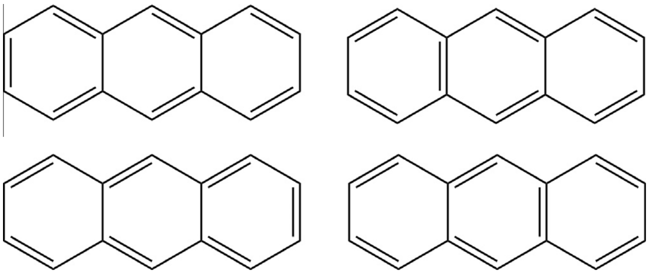

Fig. 1. The four Kekule structures of anthracene. The two at the left have conjugated 14-circuits around the perimeter.

Table 1
Experimental Enthalpies of Formation at 298.15 K in kJ/mol for all molecules used in this work.

Formula	Name	$\Delta_f H^o$ [a]	Uncertainty[b]
C_2H_4	Ethylene	+52.4	±0.5
C_4H_6	*s-trans*-Butadiene	+110.0	±0.8
C_6H_6	Benzene	+82.9	±0.9
$C_{10}H_8$	Naphthalene	+150.6	±1.1
$C_{14}H_{10}$	Anthracene	+230.9	±2.9
$C_{14}H_{10}$	Phenanthrene	+201.7[c]	±2.9
$C_{16}H_{10}$	Pyrene	+225.7	±2.5

[a] All values in this column from Ref. [9] except phenanthrene.
[b] Ref. [10].
[c] Ref. [11].

2. Benzene

As can be seen from Fig. 4, an isodesmic reaction for benzene is

$$3C_4H_6^{cis} - 3C_2H_4 \rightarrow C_6H_6 \qquad (2)$$

The left hand side of this equation just cancels all of the bonds in benzene, so the enthalpy change of this reaction should exactly equal R_1, the aromatic stabilization due to conjugation around a benzene ring. The only problem is that this reaction refers to the *s-cis* isomer of butadiene rather than the *s-trans* isomer included in Table 1. The *s-cis* isomer is highly strained due to repulsion between the cis hydrogens on the end carbon atoms. What is needed to carry out the evaluation of R_1 is hypothetical "unstrained *s-cis*-butadiene".

Accordingly here we resort to calculations. The total energy of either isomer of butadiene can be approximately separated into a sigma and a pi portion. It is assumed that the effects of strain primarily can be included in the sigma portion. Therefore the enthalpy of formation of unstrained *cis*-butadiene can be approximated by adding its pi energy to the sigma portion of unstrained *trans*-butadiene. The pi-electron energies of *cis* and *trans* butadiene can be calculated quite accurately using a semiempirical program [12,13] designed to fit high level ab initio calculations on stretched ethylene. This method should be especially accurate for computing energy differences between isomeric structures since any systematic error will likely cancel out. Table 2 gives the results for the pi-electron energies along with the derived enthalpy of formation of *s-cis*-butadiene.

Using the enthalpies of formation of benzene and ethylene from Table 1 along with that of *s-cis*-butadiene from Table 2, Eq. (2) then gives

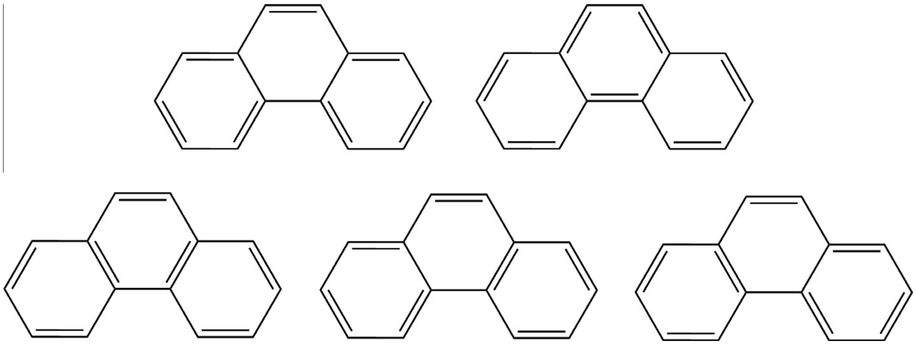

Fig. 2. The five Kekule structures of phenanthrene. The top two have conjugated 14-circuits around the perimeter.

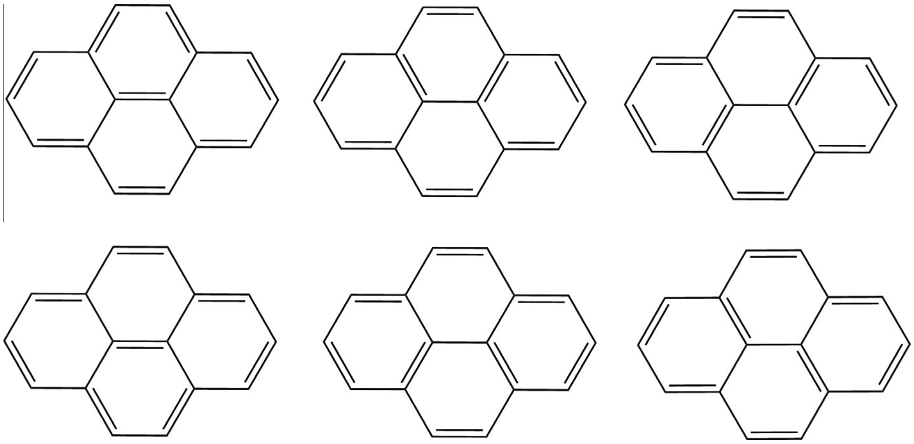

Fig. 3. The six Kekule structures of pyrene. The two at the left have conjugated 14-circuits around the perimeter.