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# Resonance Energy of an Arene Hydrocarbon from Heat of Combustion Measurements

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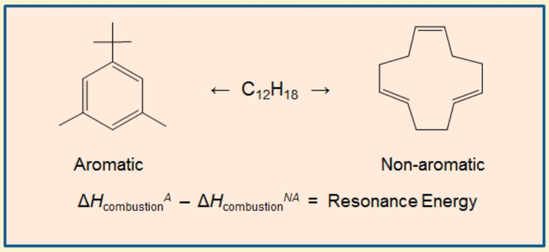
Ⓢ *Supporting Information*

**ABSTRACT:** A simple experimental method for determination of the resonance energy by measuring the energies of combustion for two isomeric compounds, aromatic 1-*tert*-butyl-3,5-dimethylbenzene and nonaromatic *trans,trans,cis*-1,5,9-cyclododecatriene is proposed. Both compounds not only have the same molecular formula, but also contain the same number of $sp^2$ and $sp^3$ carbon atoms. After converting the obtained values into the gas phase heats of combustion and subtracting one value from another, the resulting mean resonance energy of 184 kJ/mol was obtained. The proposed method can be offered as an experiment for an undergraduate physical chemistry lab curriculum.



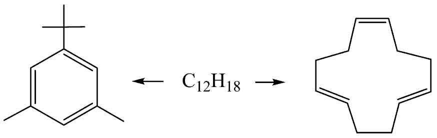
**KEYWORDS:** *Upper-Division Undergraduate, Physical Chemistry, Aromatic Compounds, Calorimetry/Thermochemistry, Organic Chemistry*

The best known and widely cited method for determining the resonance energy of aromatic hydrocarbons is based on measurement of the heats of hydrogenation of benzene and cyclohexene.[1] The heat of hydrogenation for cyclohexene is then tripled to adjust for imaginary cyclohexatriene and subtracted from $\Delta_H H$ of benzene, yielding the value of 151 kJ/mol for the resonance energy.[2] Among other empirical methods for determining the resonance energy, the heat of combustion method appears simple and accurate enough to be introduced as an undergraduate-level physical chemistry laboratory experiment. The original method[3] consisted of comparing the experimentally determined heats of combustion for benzene and cyclooctatetraene and adjusting for the difference in their composition. Subtracting the adjusted $\Delta_c H$ of cyclooctatetraene from $\Delta_c H$ of benzene gives the value of the resonance energy as 100 kJ/mol, and the value correction for conjugation (which exists to some extent in cyclooctatetraene) gives a value as 117 kJ/mol. This method suffers from necessitating tedious sample preparation for preventing loss due to evaporation, and the need to handle toxic benzene and unstable, foul-smelling and expensive cyclooctatetraene.

The aforementioned drawbacks of the combustion method were eliminated in a newer procedure[4] which suggested the use of readily available *trans,trans,cis*-1,5,9-cyclododecatriene (CDDT), whose evaporation losses are negligible thanks to its normal boiling point of 231 °C. The experimentally obtained heat of combustion for this substance was compared to the sum of heats of combustion for benzene and cyclohexane taken from the literature. It was possible because the number of carbon and hydrogen atoms in CDDT, $C_{12}H_{18}$, as well as the number of $\sigma$- and $\pi$-bonds in this substance and in the imaginary molecule composed of benzene and cyclohexane ($C_6H_6 + C_6H_{12} = C_{12}H_{18}$) is the same. The difference between the two $\Delta_c H$ yielded the median value of 130 kJ/mol for the resonance energy. This method became very popular as a bomb calorimetry experiment in the undergraduate physical chemistry lab curriculum.[5]

Significant difference in the resonance energy obtained by different empirical methods and large discrepancy between these data and theoretical resonance energy of 260 kJ/mol[6] motivated us to search for an alternative method where heats of combustion for both, aromatic and nonaromatic counterparts, would be obtained experimentally. In this paper, we report a modification of the method involving a nonconjugated macrocyclic triene, CDDT. Its heat of combustion will be measured and compared with the experimentally determined heat of combustion for 1-*tert*-butyl-3,5-dimethylbenzene (TBDMB). TBDMB has the same formula $C_{12}H_{18}$, and contains the same number of $\sigma$ and $\pi$ carbon−carbon bonds as CDDT (Scheme 1), but it is aromatic. The proposed benzene homologue TBDMB has a high boiling point of 206 °C, is not a known carcinogen, and is sold by Aldrich for an affordable price.

**Scheme 1. Structures of Aromatic and Nonaromatic Isomers of $C_{12}H_{18}$**



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## EXPERIMENTAL SECTION

Heats of combustion were determined using a PARR 1341 bomb calorimeter and Fisher Scientific Traceable digital thermometer with the resolution of 0.001°. Heat capacity of the calorimeter was determined by combustion of benzoic acid. Prior to each combustion, the samples, ~0.9 g, of both hydrocarbons CDDT and TBDMB (Aldrich, 98% pure) were loaded and the bomb was purged three times with oxygen at 30 atm pressure. In the blank test, a sample of TBDMB was placed in the bomb, purged three times as usual, and then the bomb was opened and the sample was reweighed. The mass change was 0.1 mg which is within the error of analytical balance.

## RESULTS AND DISCUSSION

The mean values of heat of combustion were determined to be −7282 and −7100 kJ/mol for CDDT and TBDMB, respectively. After Trouton's rule[7] was applied to compute the heats of vaporization of 44.3 and 42.1 kJ/mol for both substances, the gas phase heats of combustion were obtained (Scheme 2).

**Scheme 2. Thermodynamic Cycle Involving Combustion and Phase Transition Processes**

$$\begin{tikzcd}
\boxed{C_{12}H_{18}(liq) + {}^{33}/_{2}O_2} \arrow[r, "\Delta_cH^{exp}"] \arrow[d, "\Delta_{vap}H^{hc}"'] & \boxed{12CO_2 + 9H_2O(liq)} \\
\boxed{C_{12}H_{18}(gas) + {}^{33}/_{2}O_2} \arrow[r, "\Delta_cH^{gas}"] & \boxed{12CO_2 + 9H_2O(gas)} \arrow[u, "-9\Delta_{vap}H^{aq}"']
\end{tikzcd}$$

$$\Delta_cH^{gas} = \Delta_cH^{exp} - \Delta_{vap}H^{hc} + 9\Delta_{vap}H^{aq}$$

After $\Delta_cH^{gas}$ (CDDT) was subtracted from $\Delta_cH^{gas}$ (TBDMB), the value of 184 ± 4 kJ/mol was obtained (computed from 9 data sets at a confidence level of 95%); $S$ = 5.34, and RSD = 2.9%.

Alternatively, we calculated the resonance energy using the available from literature experimentally determined heats of combustion $\Delta_cH^\circ_1$ of −7324.5 and −7148.1 kJ/mol and heats of vaporization $\Delta_{vap}H^\circ$ of 67.20 and 56.63 kJ/mol for CDDT[8] and TBDMB,[9] respectively, and this results in the resonance energy of 187 kJ/mol, which is within the span of our result.

Although our resonance energy is greater than previously reported values, we have more confidence in this value because the two compounds involved are isomers and because it was computed using data entirely from the same experiment, so that any possibly present determinant error has a good chance of canceling out. There is another question of whether this result's interpretation can be extended to unsubstituted or other substituted benzene derivatives. Nonaromatic triene CDDT can be presumed free of any significant strain due to its macrocyclic structure which is able to adopt many different conformations. This hypothesis is supported by literature data: the heat of combustion for this *cis,trans,trans*-CDDT is similar to heat of combustion for all-*trans* isomer[8] (−7324.5 vs −7321.2 kJ/mol, respectively). Thermochemical properties of the aromatic counterpart, TBDMB, along with other *tert*-butylbenzenes were systematically studied.[9] Standard molar enthalpies of formation for these compounds were calculated from calorimetrically measured enthalpies of combustion and enthalpies of vaporization. The strain of a molecule was determined as the difference between the experimental $\Delta_fH^\circ$ and the calculated sum of the strain-free Benson type increments for this molecule.[9] The strain energy was found to be 9.97 kJ/mol for TBDMB, which suggests that the resonance energy determined in this work is lower than the "actual" value for a strain-free arene. Resonance energy which we calculated from these data for a hypothetical unstrained TBDMB and CDDT[8] is 197 kJ/mol. This result, however, should be considered with caution because the values referenced above were adopted from different sources.

Proposed experiment requires at least three measurements including the bomb calibration and one run for each, CDDT and TBDMB (Supporting Information). The actual time permits for one additional run per hydrocarbon, so that 3 h lab period is not exceeded. Any error associated with bomb calibration would be canceled out after subtracting the obtained heats of combustion from one another. The resonance energy calculated from the experimental data in this experiment entirely rather than using an imaginary (benzene + cyclohexane or cyclohexatriene) value appears to be more convincing for many students.

## ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00632.

Student handout/lab manual (PDF)

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### Notes

The authors declare no competing financial interest.

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