

Combustion Calorimetry of Dimethyldihydropyrene—A Carbon Bridged [14]Annulene[†]

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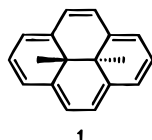
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Introduction

“Aromaticity” is a very familiar concept in chemistry textbooks. Nevertheless, its physical understanding is still somewhat ambiguous, because the only methods to measure aromatic character are indirect. There are many debates on the concept of aromaticity in the literature.¹ Aromaticity is a quantity which should be measured in energy terms and thus should be discussed in terms of the bond energies of the so-called aromatic compounds. In this sense, formation enthalpy can provide a truly critical measure of aromaticity.

The carbon-bridged [14]annulene, *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (DMDHP, **1**), is in the Hück-



el $[4n + 2]$ aromatic annulene series with $n = 3$. DMDHP is one of the molecules whereby we can deepen our understanding of aromaticity.² It is known that DMDHP has a planar peripheral ring without bond alternation and shows a large diamagnetic shielding of its methyl protons ($\delta_{\text{Me}} = -4.25$ ppm). This indicates that the π -electrons in DMDHP are well delocalized; DMDHP also has a large diamagnetic susceptibility exaltation.³ DMDHP thus meets all the magnetic criteria for aromaticity. In the present study we measure the combustion energy of DMDHP by a microbomb combustion calorimeter in order to provide an energetic reference point.

Experimental Section

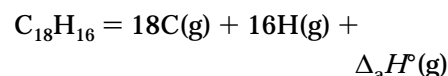
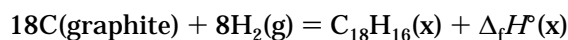
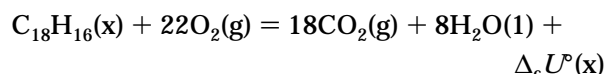
The DMDHP sample used in the present work was prepared and purified at the University of Victoria.⁴ The ¹H NMR analysis of DMDHP solution in CDCl₃ showed some tiny signals in addition to those of DMDHP. All of these additional signals were, however, due to the photo-valence isomer of DMDHP, 8,16-dimethyl[2,2]metacyclophane-4,9-diene, which is produced by visible light irradiation of DMDHP in the gas phase or in solution.⁵ We concluded that the sample was free from impurities.

Details of the combustion calorimeter used in the present study are described elsewhere.⁶ The single valve microbomb is equipped with a small platinum internal heater under the combustion crucible. Complete combustion is achieved by supplying electric energy to the internal heater during combustion. Electric current and voltage for heating were measured by two digital multimeters with transient memories. The energy equivalent of the empty calorimeter and a correction factor for the measured electric energy supplied to the internal heater were determined by burning 20 mg of thermochemical standard benzoic acid (NIST SRM 39i) under certificate conditions. The mean and standard deviation of the observed energy equivalents was 1370.12 ± 0.20 J·K⁻¹ from six calibration runs.

The result of each combustion run is shown in Table 1. The DMDHP sample was formed into 12–18 mg pellets for each combustion and burned under an oxygen pressure of 3.04 MPa in the presence of 24 mg of water in the microbomb. On each combustion run, 60 J of electric energy was supplied to the internal heater to achieve complete combustion. No carbon soot was detected by visual observation of the crucible and no carbon monoxide was detected from the bomb gas after combustion. The amount of nitric acid, which was formed by the oxidation of nitrogen impurity contained in the oxygen gas, was determined by UV spectrometry of the bomb solution. The contribution of enthalpies of formation and solution of the nitric acid to the calorimetry was taken into account. The density and specific heat capacity of DMDHP were taken to be 1.19 g·cm⁻³ from X-ray diffraction and 1.045 from DSC results, respectively, for the buoyancy correction and for the reduction of the experimental results to the standard state values. Standard specific energy of combustion, $\Delta_c U^\circ$, of the polyethylene fuse was $-46\,305$ J·g⁻¹.

Results

From the results shown in Table 1, the specific energy of combustion of DMDHP, $\Delta_c U^\circ(\text{c})$, is derived to be -9591.1 ± 1.4 J·g⁻¹, where the uncertainty is the standard deviation of the mean. Standard thermodynamic quantities of DMDHP at 298.15 K are shown in Table 2, where the uncertainties are twice the final overall standard deviation of the mean according to the rule of error propagation. Reduction to the standard state was carried out by following the literature procedure.⁷ The values of $\Delta_c U^\circ(\text{x})$, $\Delta_f H^\circ(\text{x})$, and $\Delta_a H^\circ(\text{g})$, where $\text{x} = \text{c}$ or g , refer to the following reactions, respectively.



The CODATA recommended standard formation enthalpies of CO₂(g), -393.51 ± 0.13 kJ·mol⁻¹, and of H₂O(g), -285.830 ± 0.042 kJ·mol⁻¹, were used for calculation of $\Delta_f H^\circ(\text{c})$, and those of C(g), 716.67 ± 0.44 kJ·mol⁻¹, and H(g), 217.997 ± 0.006 kJ·mol⁻¹, were used for calculation of $\Delta_a H^\circ(\text{g})$.⁸

No experimental sublimation enthalpy of DMDHP has been reported before. The isomerization of DMDHP mentioned above may lead to an erroneous experimental sublimation enthalpy. We thus estimated the sublima-

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(1) See, for example, Hiberty, P. C.; Danovich, D.; Shurki, A.; Shaik, S. *J. Am. Chem. Soc.* **1995**, *117*, 7760–7768 and references cited therein.

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(5) Blatmann, H.-R.; Schmidt, W. *Tetrahedron* **1970**, *26*, 5885–5899.

(6) Sakiyama, M.; Kiyobayashi, T. submitted to *J. Chem. Thermodyn.*

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(8) CODATA Committee on Key Values for Thermodynamics *J. Chem. Thermodyn.* **1978**, *10*, 903–906.

Table 1. Results of Combustion Calorimetry of DMDHP^a

expt no.	1	2	3	4	5	6	7
<i>m</i> (compd)/mg	12.6416	14.1021	12.3004	13.6510	13.8600	12.8807	18.3173
<i>m</i> (fuse)/mg	0.1435	0.1541	0.1668	0.1808	0.1407	0.1622	0.2268
<i>n</i> (HNO ₃)/μmol	0.994	0.800	0.852	0.352	0.785	0.576	0.563
$\epsilon^i/\text{J}\cdot\text{K}^{-1}$	0.351	0.353	0.350	0.352	0.352	0.351	0.359
$\epsilon^f/\text{J}\cdot\text{K}^{-1}$	0.372	0.376	0.371	0.375	0.376	0.373	0.389
(<i>T</i> _i - 273.15)/K	24.59189	24.59229	24.59191	24.59393	24.59397	24.59132	24.59311
(<i>T</i> _f - 273.15)/K	25.09629	25.13139	25.08759	25.12432	25.12824	25.09884	25.23828
$\Delta T_c/\text{mK}$	74.02	66.57	76.03	69.39	68.82	72.89	42.36
$\Delta T_{ad}/\text{mK}$	430.39	472.54	419.64	461.00	465.46	434.63	602.81
<i>E</i> _{ign} /J	0.149	0.126	0.121	0.145	0.134	0.168	0.108
<i>E</i> _{el} /J	60.583	58.103	59.108	59.635	58.756	55.860	58.509
- $\Delta_{\text{IBP}} U/\text{J}$	529.100	589.368	515.880	572.011	579.007	539.621	767.529
$\Delta U(\text{HNO}_3)/\text{J}$	0.059	0.048	0.051	0.021	0.047	0.034	0.034
$\Delta U_s/\text{J}$	0.279	0.316	0.271	0.305	0.310	0.286	0.427
$-\Delta_c u^o(c)/\text{J}\cdot\text{g}^{-1}$	41301.4	41261.1	41286.0	41265.3	41279.6	41285.8	41303.4
$-\Delta_c U^o(c)/\text{kJ}\cdot\text{mol}^{-1}$	9595.36	9586.00	9591.77	9586.96	9590.29	9591.73	9595.81

^a *m*(compd), sample mass; *m*(fuse), mass of polyethylene fuse; *n*(HNO₃), amount of HNO₃; ϵ^i energy equivalent of the bomb contents in the initial state; ϵ^f , energy equivalent of the bomb contents in the final state; *T*_i, initial temperature of the reaction period; *T*_f, final temperature of the reaction period; ΔT_c : correction to the temperature rise; ΔT_{ad} , Adiabatic temperature rise; *E*_{ign}, ignition energy; *E*_{el}, electric energy to the internal microheater; IBP, isothermal bomb process; $\Delta U(\text{HNO}_3)$, energy change associated with the formation of HNO₃; ΔU_s , Standard-state correction; $\Delta_c u^o(c)$, standard specific energy of combustion; $\Delta_c U^o(c)$, standard molar energy of combustion.

Table 2. Standard Thermodynamic Quantities of DMDHP at 298.15 K

$\Delta_c u^o(c)/\text{J}\cdot\text{g}^{-1}$	-41283 ± 17
$\Delta_c U^o(c)/\text{kJ}\cdot\text{mol}^{-1}$	-9591.1 ± 4.0
$\Delta_c H^o(c)/\text{kJ}\cdot\text{mol}^{-1}$	-9601.1 ± 4.0
$\Delta_f H^o(c)/\text{kJ}\cdot\text{mol}^{-1}$	231.2 ± 4.6
$\Delta_{\text{sub}} H^o(c)/\text{kJ}\cdot\text{mol}^{-1}$	107.6 ± 1.7 ^a
$\Delta_f H^o(g)/\text{kJ}\cdot\text{mol}^{-1}$	338.8 ± 4.9
$\Delta_a H^o(g)/\text{kJ}\cdot\text{mol}^{-1}$	16 049.1 ± 9.3

^a Estimated by an empirical atom-atom potential with crystal structure determined by X-ray diffraction.

tion enthalpy by an empirical nonbonded C-C and C-H potential proposed by Williams⁹ on the basis of the crystal structure determined by X-ray diffraction. Averaging the values calculated with five parameter sets (sets I-V; these are for both aromatic and nonaromatic compounds), we get the lattice energy, *E*, of DMDHP as 105.1 ± 1.7

kJ·mol⁻¹. Hence we estimated the sublimation enthalpy of DMDHP at 298.15 K as $E + RT = 107.6 \pm 1.7$ kJ·mol⁻¹. This value and the formation enthalpy in the crystalline state give the formation enthalpy of DMDHP in the gaseous state as 338.8 ± 4.9 kJ·mol⁻¹.

We now have experimental formation enthalpies for two planar annulenes, benzene ([6]annulene) and DM-DHP ([14]annulene). If we can extend the experimental measurements on other series of annulenes, we will be able to provide a basis for determining the experimental resonance energy of annulene and deepen our knowledge of aromaticity.

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