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A R T I C L E S

The Aromaticity of Pyracylene: An Experimental and Computational Study of the Energetics of the Hydrogenation of Acenaphthylene and Pyracylene

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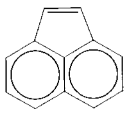
Abstract: In this work, the aromaticity of pyracylene (**2**) was investigated from an energetic point of view. The standard enthalpy of hydrogenation of acenaphthylene (**1**) to acenaphthene (**3**) at 298.15 K was determined to be −(114.5 ± 4.2) kJ mol^{-1} in toluene solution and −(107.9 ± 4.2) kJ mol^{-1} in the gas phase, by combining results of combustion and reaction−solution calorimetry. A direct calorimetric measurement of the standard enthalpy of hydrogenation of pyracylene (**2**) to pyracene (**4**) in toluene at 298.15 K gave −(249.9 ± 4.6) kJ mol^{-1}. The corresponding enthalpy of hydrogenation in the gas phase, computed from the $\Delta_f H^o_m$(cr) and $\Delta_{sub} H^o_m$ values obtained in this work for **2** and **4**, was −(236.0 ± 7.0) kJ mol^{-1}. Molecular mechanics calculations (MM3) led to $\Delta_{hyd} H^o_m$(**1**,g) = −110.9 kJ mol^{-1} and $\Delta_{hyd} H^o_m$(**2**,g) = −249.3 kJ mol^{-1} at 298.15 K. Density functional theory calculations [B3LYP/6-311+G(3d,2p)//B3LYP/6-31G(d)] provided $\Delta_{hyd} H^o_m$(**2**,g) = −(244.6 ± 8.9) kJ mol^{-1} at 298.15 K. The results are put in perspective with discussions concerning the “aromaticity” of pyracylene. It is concluded that, on energetic grounds, pyracylene is a borderline case in terms of aromaticity/antiaromaticity character.

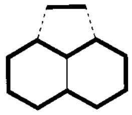
Introduction

Acenaphthylene (**1**) and pyracylene (**2**) have been among the cornerstones in discussions of “aromaticity” concepts.[1−5] According to Craig’s rules, both **1** and **2** are aromatic.[1] In terms of the $4n + 2$ rule, acenaphthylene is also considered an “aromatic” molecule composed of a 10-π-electron naphthalene core connected to a 2-π-electron etheno system (**1a**). The $4n + 2$ rule predicts pyracylene to be “aromatic” if it is regarded as a 10-π-electron naphthalene unit connected to two 2-π-electron etheno systems (**2a**) but “antiaromatic” if it is viewed as a 12-π-electron cyclododecahexaene periphery perturbed by an internal cross-linked etheno unit (**2b**).

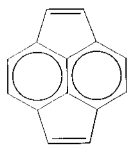


1

Acenaphthylene

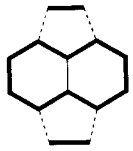


1a

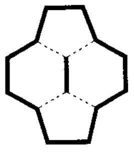


2

Pyracylene



2a



2b

Which of the two limiting structures, **2a** or **2b**, best represents pyracylene, and the question of its “aromatic” or “antiaromatic” character, has been a matter of debate[6−14] since the compound was first synthesized by Trost and co-workers.[6] Analysis of the magnetic properties of pyracylene was taken to favor model **2b**. For example, the ^{1}H NMR signals of **2** appear at relatively

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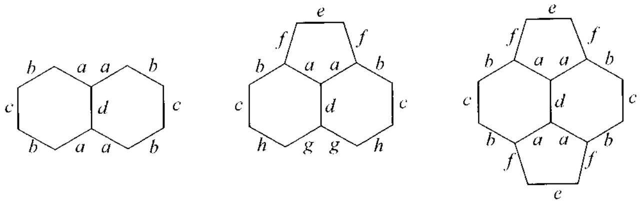
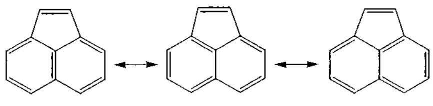


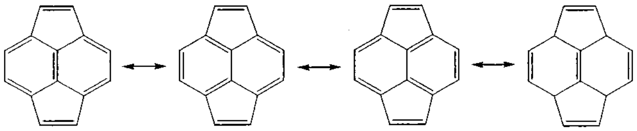
Figure 1. C−C bond distances (pm) in naphthalene, acenaphthylene, and pyracylene. Naphthalene: $a = 142.6$, $b = 137.8$, $c = 141.5$, $d = 142.6$.[21] Acenaphthylene: $a = 144.1$, $b = 138.1$, $c = 142.4$, $d = 138.6$, $e = 139.5$, $f = 146.6$, $g = 143.3$, $h = 138.2$.[20] Pyracylene: $a = 139.7$, $b = 137.9$, $c = 144.3$, $d = 136.0$, $e = 134.6$, $f = 149.2$.[15]

high field ($\delta = 6.01$ and 6.52 ppm in CCl_4),[6b] indicating the presence of some induced paramagnetic ring current. This paratropic shift, although moderate when compared with that observed in ^{1}H NMR spectra of other bridged [4*n*]annulenes,[15] is predicted for “antiaromatic” systems[2,3,16] and is therefore consistent with pyracylene being a perturbed “antiaromatic” [12]-annulene.[4] Theoretical calculations of the π-electron magnetic properties of pyracylene support this view[9,13,17] and suggest that the paratropism is mainly associated with the five-membered rings.[9,13,17,18] In contrast, no significant paratropic shift is observed for acenaphthylene, whose ^{1}H NMR signals ($\delta = 7.072$, 7.535, 7.676, and 7.796 ppm in $CDCl_3$)[19] show chemical shifts in a range similar to those of naphthalene ($\delta = 7.841$ and 7.475 ppm in $CDCl_3$; $\delta = 7.671$ and 7.316 ppm in CCl_4).[19]

Structural criteria, on the other hand, seem to favor model **2a** for pyracylene. It was expected that if **2** could be regarded as an “antiaromatic” [12]annulene (**2b**), the bridging central double bond should exert only a very small perturbation upon the 12π periphery of the ring system, and that the steric constraints should reduce the ability of the molecule to relieve unfavorable electronic interactions by bond length alternation.[6] The X-ray structure of **2** revealed, however, that the molecule exhibits pronounced bond length alternation along the molecular periphery, with a considerable bond fixation in the etheno bridges fused to the naphthalene fragment (Figure 1).[15] This fixation is even greater than that observed for acenaphthylene,[20] whose naphthalene core also shows a somewhat less pronounced deviation in bond distances relative to those found in naphthalene itself [21] (Figure 1). Interestingly, the opposite might be expected by considering the principal canonical forms **1b**−**1d** and **2c**−**2f** of the two molecules. Forms **1b**−**1d** of acenaphthylene, with a bridging double bond, have their counterparts in forms **2c**−**2e** of pyracylene, but an additional structure, **2f**, with a bridging single bond, can be drawn for pyracylene. As previously noted,[15] the fact that a greater bond fixation is experimentally observed in **2** suggests that form **2f** contributes negatively to the structure count in pyracylene, as predicted by Herndon’s theory.[22]

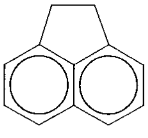


1b **1c** **1d**



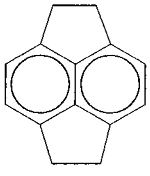
2c **2d** **2e** **2f**

If the naphthalene moiety retained its “aromaticity” in compounds **1** and **2**, and the etheno bridges in **1** and **2** did not interact significantly with the naphthalene double bonds, one would expect $\Delta_{\text{hyd}}H^{\text{o}}_{\text{m}} \approx -110$ kJ mol^{-1} for the hydrogenation of acenaphthylene to acenaphthene (**3**) and twice that amount, $\Delta_{\text{hyd}}H^{\text{o}}_{\text{m}} \approx -220$ kJ mol^{-1}, for the hydrogenation of pyracylene to pyracene (**4**) at 298.15 K. Both of these estimates are based on $\Delta_{\text{hyd}}H^{\text{o}}_{\text{m}} = -(110.4 \pm 1.6)$ kJ mol^{-1} for cyclopentene at 298.15 K in the gas phase.[23]



3

Acenaphthene



4

Pyracene

In this work, we have determined the energetics of the hydrogenation of **1** to **3** and of **2** to **4** using combustion calorimetry, reaction−solution calorimetry, hydrogenation calorimetry, Calvet drop sublimation calorimetry, and Knudsen effusion vapor pressure versus temperature measurements. The results are compared with those of molecular mechanics and density functional theory calculations. Thermochemical, structural, and NMR data are now available for compounds **1**−**4**, but, not surprisingly,[24] there is no clear-cut answer regarding the “aromatic” or “antiaromatic” character of pyracylene.

Methods

Gas chromatographic (GC) analyses were carried out using a Hewlett-Packard 8500 apparatus equipped with a methyl−5% phenyl silicone capillary column (25 m, 5 μm diameter) and a flame ionization

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detector. Temperature program: initial temperature 373 K, 5 min; program rate 10 K min^{-1}; final temperature 493 K. Injection temperature 423 K, detection temperature 573 K.

Heat capacity measurements on **4** were made with a DSC 7 from Perkin-Elmer in the temperature range 288.15−308.15 K (scan rate 5 K min^{-1}). Sapphire and benzoic acid were used as references.

Materials. Acenaphthylene and acenaphthene (both Fluka, purum) were purified by several recrystallizations from petroleum ether and sublimation. GC analysis gave purities of 99% for acenaphthene and >99.95% for acenaphthylene. Pyracylene was prepared and purified as previously described.[15] Pyracene was synthesized by catalytic hydrogenation of pyracylene. Pyracylene of highest purity should be used, as the removal of impurities (especially pyrene) after hydrogenation is difficult. A catalytic amount of 10% Pt/C (Fluka, "puriss. Hydrierungskatalysator") was added to a solution of 200 mg (1.44 mmol) of pyracylene in 150 mL of hexane (Fluka, "puriss. p.a."). The mixture was shaken under a hydrogen atmosphere until it ceased to absorb H_2 and became essentially colorless. The solution was filtered through a short column of silica gel (Fluka, 0.035−0.070 mm) to remove the catalyst. The off-white solid residue left by evaporation was dissolved in warm acetone, and the solution was treated with charcoal and filtered. Pyracene was precipitated in the cold and recrystallized from hexane at 253 K. ^{1}H NMR, UV/vis, and elemental analysis (Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.38; H, 6.91.) of the white, crystalline product (mp 489.7−490.7 K; lit. mp 487.2−490.2 K,[25] 487.7−490.7 K[26]) gave no indication of impurities. The purity of the pyracene sample determined by GC analysis was >99.5%. A trace impurity absorbing at longer wavelengths ($\lambda_{\mathrm{max,exc}} =$ 343 nm) than pyracylene was detected by fluorescence spectroscopy ($\lambda_{\mathrm{max,em}} =$ 392 nm). The sample was sublimed prior to combustion.

Combustion Calorimetry. The standard energies of combustion of acenaphthene, acenaphthylene, pyracene, and pyracylene were measured using a microcombustion calorimeter. Details of the apparatus and the general experimental procedure have been described.[27] In a typical experiment, a pellet of the compound under study (ca. 7−38 mg) and a drop (ca. 2−7 mg) of *n*-hexadecane (B.D.H.) were placed in a Pt crucible and weighed to 0.1 μg in a Sartorius 4504 Mp8-1 ultramicrobalance. This sample was burned under 3.04 MPa of oxygen (ArLíquido N45, mass fraction > 0.9995) with 50 μL of distilled and deionized water inside the stainless steel bomb of 17.95 cm^3 internal volume. The HNO_3 formed from traces of atmospheric N_2 inside the bomb was determined as NO_3^- using a Dionex 4000i ion chromatography apparatus. The mass of carbon residue found in the crucible at the end of some of the experiments was gravimetrically determined.[28]

Reaction−Solution Calorimetry. The isoperibol reaction−solution calorimeter used to measure the enthalpies of solution of acenaphthylene and acenaphthene in toluene was essentially identical to the versions previously described.[29] In a typical experiment, a thin-walled glass ampule was loaded with the sample and weighed to $\pm 10^{-5}$ g on a Mettler AT201 balance. The masses of sample were in the range 249−422 mg in the case of acenaphthylene and 166−195 mg in the case of acenaphthene. The calorimetric vessel (a transparent Dewar vessel) was filled with 125 mL of toluene (Merck p.a.), which had been dried and distilled under sodium benzophenone ketyl, and kept under N_2 atmosphere prior to use. The energy equivalent of the calorimeter was determined by electrical calibration. The calibration immediately preceded the dissolution process, which was started by breaking the glass ampule containing the sample in the calorimetric solvent.

Hydrogenation Calorimetry. The enthalpy of hydrogenation of pyracylene in toluene at 298.15 K was determined using the isoperibol hydrogenation calorimeter previously reported.[30] Between 13 and 25 mg of pyracylene was weighed with an accuracy of ± 2 μg in a Sartorius MP3 microbalance and dissolved in 500 μL of toluene (Aldrich, 99+%). The resulting solution (3−6% w/w) had a blood-red color and stained filter paper brown. Upon dissolution, what appeared to be one or two small yellow or colorless crystals remained in the sample tube. Debris of this kind was also observed as a nonvolatile and insoluble remainder when pyracylene crystals were sublimed (see Sublimation Calorimetry below). We believe the weight of this trace contaminant to be negligible within the error limits stated for the experimental results. Toluene was selected as the solvent after attempts with hexane, tetrahydrofuran, and 50/50 (v/v) hexane−THF proved unsuccessful due to insufficient solubility. An amount of styrene thermochemically equivalent to the pyracylene solution was dissolved in 500 μL of toluene. Thermochemical equivalence, that is, a concentration of sample and calibrant that produces roughly the same amount of heat on hydrogenation, was established by a preliminary experiment and required $n(\mathbf{5})/n(\mathbf{2}) \approx 2$, where *n* represents the amount of substance. The calorimetric vessel contained a suspension of 300 mg of 5% Pd−C catalyst (Aldrich) in 18.0 mL of toluene (Aldrich, 99+%), stirred magnetically at 350 rpm. Hydrogen at a pressure of 0.1 MPa over ambient was conveyed through a septum into the vessel by means of a hypodermic needle. Catalyst activation (adsorption of H_2) took place with heat evolution. As a result, the calorimeter temperature increased by 1 K or more over a period of 15−20 min. The recording of the voltage−time curve for the pyracylene hydrogenation experiment was started. At the end of the initial period, 20.0 μL of the 3−6% (w/w) solution mentioned above was injected into the calorimetric vessel. Injections were made with a GC microsyringe fitted with a Cheyney adaptor for maximum reproducibility. The hydrogenation of pyracylene was followed by a calibration run where 20 μL of the styrene solution was injected in the calorimetric vessel. The enthalpy of hydrogenation of pyracylene, $\Delta_{\mathrm{hyd}}H^{\mathrm{o}}_{\mathrm{m}}(\mathbf{2})$, was calculated from eq 1, where *n* represents the amount of substance, ΔV_{ad} is a voltage change proportional to the adiabatic temperature rise, and

$$\Delta_{\mathrm{hyd}}H^{\mathrm{o}}_{\mathrm{m}}(\mathbf{2}) = \Delta_{\mathrm{hyd}}H^{\mathrm{o}}_{\mathrm{m}}(\mathbf{5})\frac{n(\mathbf{5})\Delta V_{\mathrm{ad}}(\mathbf{2})}{n(\mathbf{2})\Delta V_{\mathrm{ad}}(\mathbf{5})} \qquad (1)$$

$\Delta_{\mathrm{hyd}}H^{\mathrm{o}}_{\mathrm{m}}(\mathbf{5}) = -(118.2 \pm 0.3)$ kJ mol^{-1} is the enthalpy of hydrogenation of styrene in hexane,[31] which was assumed to be transferable to toluene. This routine was repeated nine times (18 hydrogenations in all). The entire experiment was repeated on three different days with three different sets of solutions to ensure reproducibility. The hydrogenations of pyracylene in the calorimeter were complete in about 10 s and led to colorless solutions. Upon evaporation of a small portion of the final calorimetric solution, a volatile, colorless wax or oil remained. GC−MS analysis of this residue indicated only the presence of pyracene. The quantitative hydrogenation of pyracylene to pyracene in ethyl acetate at 298.15 K under 0.1 MPa of H_2, and using platinum oxide as catalyst, was previously observed by Trost at al.[6b]

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Table 1. Energies and Enthalpies of Combustion, Enthalpies of Hydrogenation, Enthalpies of Sublimation, and Enthalpies of Formation at 298.15 K (Data in kJ mol^{-1})

compound	$-\Delta_c U^o_m$	$-\Delta_c H^o_m$	$\Delta_f H^o_m$(cr)	$\Delta_{sub} H^o_m$	$\Delta_f H^o_m$(g)	$-\Delta_{hyd} H^o_m$
acenaphthylene (**1**)	6051.3 ± 3.1	6056.2 ± 3.1	190.8 ± 3.4	72.97 ± 0.33[a]	263.8 ± 3.4	107.9 ± 4.2[b] 114.5 ± 4.2[c]
acenaphthene (**3**)	6217.1 ± 2.7	6223.3 ± 2.7	70.3 ± 2.5	85.6 ± 0.3[d]	155.9 ± 2.5	
pyracylene (**2**)	6974.1 ± 3.0	6979.1 ± 3.0	326.6 ± 3.6			
	6971.6 ± 3.1[e]	6976.6 ± 3.1[e]	324.4 ± 3.6[e]			
			325.4 ± 2.5[f]	(84.9 ± 5.0)[g]	410.3 ± 5.6	236.0 ± 7.7[h] 249.9 ± 4.6[i]
pyracene (**4**)	7301.4 ± 3.7	7308.8 ± 3.7	84.7 ± 4.1	89.6 ± 3.3	174.3 ± 5.3	

[a] Reference 46. [b] Gas phase, calculated from the enthalpies of formation of gaseous acenaphthylene and acenaphthene obtained in this work. [c] Value in toluene, calculated from the experimental data in Scheme 1. [d] Calculated in this work from the vapor pressure−temperature data given in refs 43, 47, and 48, and the heat capacity data in refs 49 and 50 (see text). [e] Reference 45. [f] Recommended; average of $\Delta_f H^\circ_m(\mathbf{2},\mathrm{cr}) = 326.6 \pm 3.6$ kJ mol^{-1} obtained in this work and $\Delta_f H^\circ_m(\mathbf{2},\mathrm{cr}) = 324.4 \pm 3.6$ kJ mol^{-1} previously reported in ref 45. [g] Estimated in ref 45. [h] Gas phase, calculated from the enthalpies of formation of gaseous pyracene and pyracylene reported in this work. [i] Experimental value in toluene obtained in this work.

Sublimation Calorimetry. Several attempts were made to determine the enthalpy of sublimation of pyracylene using a Calvet microcalorimeter adapted for the measurement of sublimation enthalpies by the vacuum-drop method.[32] Only one clean sublimation run was observed. In this case, the microcalorimeter temperature was set at 342 K. A thin capillary containing 1.1871 mg of **2** was weighed on a Sartorius 4504 Mp8-1 ultramicrobalance. The reference and sample cells, both initially empty and under argon atmosphere, were simultaneously evacuated using a pumping system whose ultimate vacuum was 4×10^{-3} Pa. The pumping background and calibration curves were recorded in sequence. Argon was admitted to the cells, and once a stable baseline was determined, the sample was dropped into the sample cell. An endothermic peak due to the heating of the sample from room temperature to 342 K was first observed. Evacuation of the cells was reinitiated after the signal returned to the baseline and the measuring curve corresponding to the sublimation of pyracylene was acquired. At the end of the experiment, the sample cell was removed from the calorimeter and its interior inspected for the presence of unsublimed or decomposed pyracylene. In this run, no decomposition residue or unsublimed sample was found inside the cell. In several other runs at the same temperature, however, small amounts of a yellowish residue were found inside the capillary at the end of the experiment.

The duration of the sublimation period varied from 4 to 6 h, and the corresponding curves were shallow and broad due to the slow sublimation of pyracylene under the experimental conditions. It was not possible, however, to increase the sublimation rate (which would lead to a sharper and easier to integrate peak) by increasing the temperature of the calorimeter. In a run with the apparatus set at 363 K, an exothermic curve, overlapping with the endothermic peak due to the heating of the sample from room temperature to 363 K, was immediately observed after the sample was dropped inside the calorimeter. No sublimation peak (endothermic) was detected after the evacuation of the cells started, and, at the end of the experiment, it was found that the sample had decomposed inside the capillary, yielding a yellowish product. A higher temperature for the onset for the thermal decomposition of solid pyracylene was determined using a Setaram DSC 121 differential scanning calorimeter. In these experiments, a mass of 2.36 mg of **2** was sealed in air inside an aluminum crucible and heated at 2 K min^{-1} in the range 333−473 K, using argon as the purging gas. The curve obtained showed a single exothermic peak corresponding to the decomposition of pyracylene, with the onset at 370.7 K. A similar result, but with the onset at 403 K, was reported by Sarobe et al.[33]

Knudsen Effusion Measurements. The Knudsen effusion apparatus previously described[34] was used to determine the enthalpy of sublimation of pyracene. The cell was charged with ca. 0.150 g of pyracene at the beginning of the experiments, and the mass loss in each run was determined to $\pm 10^{-5}$ g with a Sartorius 2474 balance.

Computations. Molecular mechanics calculations were carried out using the MM3 force field.[35] The input files were constructed using the draw function of PC MODEL.[36] Conformational searches used the method of Saunders,[37] contained in the MM3 package.[38] As a test of the search technique, a conformer search was performed on cyclononane, which has five well-documented conformers within 14.6 kJ mol^{-1} of the ground state.[39] All the conformers were found.

Density functional theory (DFT) calculations were done using the Gaussian 98 package, Revision A.7.[40] The structures were fully optimized (NOSYM) at the B3LYP/6-31G(d) level of theory. The resulting geometries were very close to the expected symmetry point groups with nearly planar carbon cores, D_{2h} for naphthalene, pyracene (**4**), and pyracylene (**2**) and C_{2v} for acenaphthene (**3**) and acenaphthylene (**1**). Insignificantly lower energies were obtained by symmetry adaptation of the coordinates and reoptimization without the NOSYM request. The predicted structural data agreed satisfactorily with X-ray results for **1** and **2** (Figure 1). The standard deviation between experimental and calculated bond lengths was 1.2 pm, and the maximum deviation was 3 pm. Calculated bond angles were within the standard deviation of the experimental data (0.3°). Single-point energies were then computed with the 6-311+G(2d,p) and 6-311+G(3df,2p) basis sets. Zero-point and thermal energy corrections (without frequency scaling) were obtained with the 6-31G(d) basis set.

Results and Discussion

The standard internal energies and enthalpies of combustion of **1**−**4** at 298.15 K obtained in the combustion calorimetric experiments are shown in Table 1. These results refer to the reaction in eq 2 (acenaphthylene, $m = 12$, $n = 8$; pyracylene,

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$m = 14$, $n = 8$; acenaphthene, $m = 12$, $n = 10$; and pyracene, $m = 14$, $n = 12$) and correspond to the mean of seven

$$C_mH_n(cr) + (m + n/4)O_2(g) \rightarrow mCO_2(g) + (n/2)H_2O(l) \quad (2)$$

experimental determinations in the case of acenaphthylene, six determinations each in the case of pyracylene and acenaphthene, and five determinations in the case of pyracene. The uncertainties quoted represent twice the overall standard deviation of the mean and include the contributions from the calibration with benzoic acid and from the energy of combustion of *n*-hexadecane.[41] The standard enthalpies of formation of **1**−**4** in the crystalline state at 298.15 K are also listed in Table 1 and were derived from the corresponding $\Delta_cH^o_m$ values using $\Delta_fH^o_m$(CO_2,g) = −(393.51 ± 0.13) kJ mol^{-1} [42] and $\Delta_fH^o_m$(H_2O,l) = −(285.830 ± 0.040) kJ mol^{-1}.[42]

The standard enthalpy of formation of crystalline acenaphthene obtained in this work, 70.3 ± 2.5 kJ mol^{-1} (Table 1), is in excellent agreement with the value 70.3 ± 3.0 kJ mol^{-1} previously measured by Boyd et al. using a macrocombustion calorimeter.[43] The published values of the standard molar enthalpy of formation of acenaphthylene in the crystalline state, 186.7 ± 4.9 kJ mol^{-1} [43] and 192.6 ± 4.3 kJ mol^{-1},[44] which were measured by macrocombustion calorimetry, also agree within the experimental errors with the present microcombustion calorimetry result of 190.8 ± 3.4 kJ mol^{-1} (Table 1). As indicated in Table 1, the redetermination of the standard enthalpy of formation of crystalline pyracylene carried out in this work led to $\Delta_fH^o_m$(**2**,cr) = 326.6 ± 3.6 kJ mol^{-1}, in excellent agreement with our previous result, $\Delta_fH^o_m$(**2**,cr) = 324.4 ± 3.6 kJ mol^{-1}.[45] The mean of these two values, $\Delta_fH^o_m$(**2**,cr) = 325.4 ± 2.5 kJ mol^{-1}, is therefore proposed for the enthalpy of formation of crystalline pyracylene.

A value of 71.2 ± 3.8 kJ mol^{-1} can be derived for the enthalpy of sublimation of acenaphthylene at 302.16 K from the Knudsen effusion results published by Boyd et al.[43] Calorimetric measurements by Morawetz gave $\Delta_{sub}H^o_m$(**1**,298.15 K) = 72.97 ± 0.33 kJ mol^{-1}.[46] The latter value was used in the present work to calculate the enthalpy of formation of gaseous acenaphthylene (Table 1).

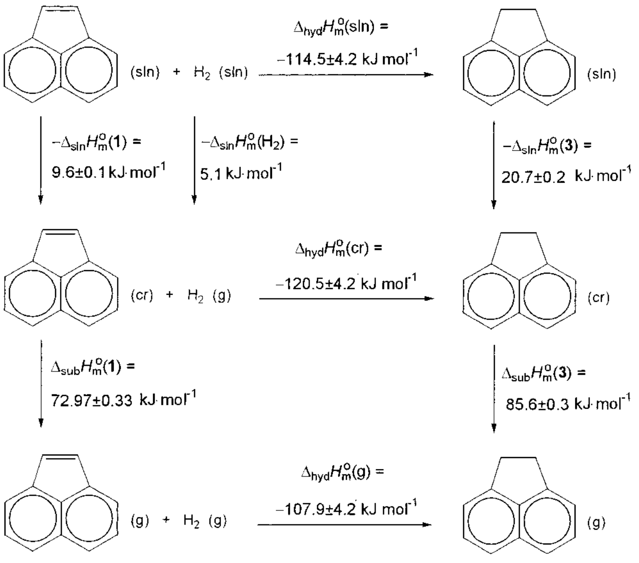
Three independent values for the enthalpy of sublimation of acenaphthene can be computed from the vapor pressure vs temperature data reported by different authors: 85.9 ± 1.9 kJ mol^{-1} at 306.89 K,[43] 83.8 ± 2.7 kJ mol^{-1} at 341.9 K,[47] and 83.6 ± 0.3 kJ mol^{-1} at 352.2 K.[48] Correction of these values to 298.15 K using eqs 3 and 4, where $\Delta_{sub}C^o_{p,m}$, represents the

$$\Delta_{sub}H^o_m(298.15\ \mathrm{K}) = \Delta_{sub}H^o_m(T) + \int_T^{298.15\ \mathrm{K}} \Delta_{sub}C^o_{p,m}\mathrm{d}T \quad (3)$$

$$\Delta_{sub}C^o_{p,m}(\mathbf{3})/(\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}) = -0.0041T^2 + 2.3185T - 355.77 \quad (4)$$

difference in heat capacity of the gaseous and crystalline compound, leads to 86.2 ± 1.9, 85.3 ± 2.7, and 85.6 ± 0.3 kJ mol^{-1}, respectively. The weighted mean of these three results, $\Delta_{sub}H^o_m$(**3**,298.15 K) = 85.6 ± 0.3 kJ mol^{-1}, was used in this work to derive the value of $\Delta_fH^o_m$(**3**,g) (Table 1). Equation 4 is based on the heat capacity data for solid and gaseous acenaphthene reported by Cheda and Westrum[49] and Kudchadker et al.,[50] respectively, in the temperature range 298.15−350.00 K.

Scheme 1



The reaction−solution calorimetric measurements of the enthalpies of solution of acenaphthylene and acenaphthene in toluene at 298.15 K led to $\Delta_{sln}H^o_m$(**1**) = 9.6 ± 0.1 kJ mol^{-1} and $\Delta_{sln}H^o_m$(**3**) = 20.7 ± 0.2 kJ mol^{-1}, where the uncertainties quoted represent twice the standard deviation of the mean of five independent measurements. These results, in conjunction with the enthalpy of solution of H_2 in toluene, $\Delta_{sln}H^o_m$(H_2) = 5.1 kJ mol^{-1},[51] and the enthalpies of formation in Table 1, lead to the enthalpies of hydrogenation of acenaphthylene, in toluene solution, in the crystalline state, and in the gas phase, indicated in Scheme 1. The values of $\Delta_{hyd}H^o_m$(**1**) in solution and in the gas phase are also shown in Table 1.

The vapor pressures, p, of pyracene obtained in the Knudsen effusion experiments were calculated from eq 5,[52,53] where m

$$p = \frac{m}{At}\left(\frac{2\pi RT}{M}\right)^{1/2}\left(\frac{8r + 3l}{8r}\right)\left(\frac{2\lambda}{2\lambda + 0.48r}\right) \quad (5)$$

is the mass loss during time t, $A = 4.404 \times 10^{-3}$ cm^2, $l = 2.09 \times 10^{-2}$ cm, and $r = 3.744 \times 10^{-2}$ cm are the area, the thickness, and the radius of the effusion hole, respectively, M is the molar mass of pyracene, R is the gas constant, T is the absolute temperature, and λ is the mean free path given by eq 6. Here k

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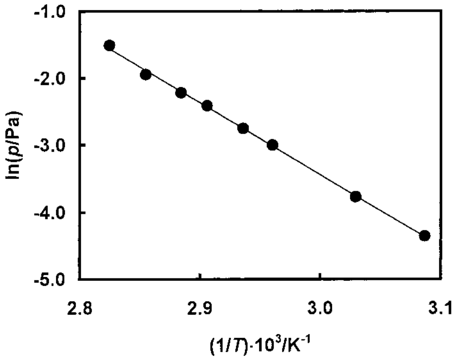

Figure 2. Vapor pressure of pyracene as a function of the temperature.

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 p} \tag{6}$$

represents the Boltzmann constant, and $\sigma = 9.06 \times 10^{-8}$ cm is the collision diameter of pyracene. The value of σ was estimated from projections of the molecular structure of pyracene[54] in the *xy*, *xz*, and *yz* planes (the van der Waals radii of the carbon and hydrogen atoms were taken into account).[55] The mean free path is pressure-dependent (eq 6), and in order to calculate the vapor pressure of pyracene through eq 5, it was necessary to use an iterative method. As a first approximation, *p* was calculated by ignoring the λ-dependent term in eq 5. The obtained result was subsequently used to derive λ from eq 6. The calculated mean free path was introduced into eq 5, and a second *p* value was calculated. This was used to derive a new λ from eq 6, and the iteration was continued until the difference between successive values of *p* was less than 10^{-8} Pa.

Least-squares fitting of eq 7[56] to the obtained vapor pressure−temperature data.

led to $a = (28.61 \pm 1.06)$ and $b = -\Delta_{\text{sub}}H^{\text{o}}_{\text{m}}/R = -(10682.10 \pm 360.33)$ K, with a regression coefficient of 0.9994. The corresponding plot of ln *p* versus $1/T$ is presented

$$\ln p = a + \frac{b}{T} \tag{7}$$

in Figure 2. The enthalpy of sublimation of pyracene at the mean temperature, $T_{\text{m}} = 339.01$ K, of the temperature range covered by the experiments, calculated from the slope *b* of eq 7, is $\Delta_{\text{sub}}H^{\text{o}}_{\text{m}}$(**4**,339.01 K) = 88.8 ± 3.0 kJ mol^{-1}. The uncertainties quoted for *a* and *b*, and the $\Delta_{\text{sub}}H^{\text{o}}_{\text{m}}$(**4**,339.01 K) values, include Student's factor for 95% confidence level ($t = 2.365$).[57] The enthalpy of sublimation of pyracene at 298.15 K can be calculated from the corresponding value at 339.01 K using eq 3, where $\Delta_{\text{sub}}C^{\text{o}}_{\text{p,m}}$ represents the difference in heat capacity of gaseous and crystalline pyracene. Combination of the value $C^{\text{o}}_{\text{p,m}}$(**4**,cr) = 215.2 J K^{-1} mol^{-1}, obtained in this work by DSC, with $C^{\text{o}}_{\text{p,m}}$(**4**,g) = 209.7 J K^{-1} mol^{-1} calculated by the DFT method (6-31G*), gives $\Delta_{\text{sub}}C^{\text{o}}_{\text{p,m}} = -5.5$ J K^{-1} mol^{-1}. A value of $\Delta_{\text{sub}}C^{\text{o}}_{\text{p,m}} = -(33.0 \pm 33.0)$ J K^{-1} mol^{-1} can also be derived from the empirical correlation in eq 8.[58] The uncertainty

$$\Delta_{\text{sub}}C^{\text{o}}_{\text{p,m}}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -0.75 - 0.15C^{\text{o}}_{\text{p,m}}(\text{cr}) \tag{8}$$

quoted for $\Delta_{\text{sub}}C^{\text{o}}_{\text{p,m}}$ is the standard deviation between the experimental values used to derive eq 8 and the corresponding estimates.[58] Using the average of the two $\Delta_{\text{sub}}C^{\text{o}}_{\text{p,m}}$ values indicated above with an assumed uncertainty of ±33.0 J K^{-1} mol^{-1} ($\Delta_{\text{sub}}C^{\text{o}}_{\text{p,m}} = 19.3 \pm 33$ J K^{-1} mol^{-1}), $\Delta_{\text{sub}}H^{\text{o}}_{\text{m}}$(**4**,298.15 K) = 89.6 ± 3.3 kJ mol^{-1} is derived (Table 1).

The only clean run in our attempts to measure the enthalpy of sublimation of pyracylene (see Experimental Section) led to $\Delta_{\text{sub}}H^{\text{o}}_{\text{m}}$(**2**) = 82.0 kJ mol^{-1} at 342 K. This value can be corrected to 298.15 K by using eq 3, where, in this case, $\Delta_{\text{sub}}C^{\text{o}}_{\text{p,m}}$ represents the difference in heat capacity of gaseous and crystalline pyracylene. Combination of the experimental value, $C^{\text{o}}_{\text{p,m}}$(**2**,cr) = 193.8 J K^{-1} mol^{-1},[45] at 298.15 K with the corresponding $C^{\text{o}}_{\text{p,m}}$(**2**,g) = 167.5 J K^{-1} mol^{-1}, calculated in this work by the DFT method (6-31G*), gives $\Delta_{\text{sub}}C^{\text{o}}_{\text{p,m}} = -26.3$ J K^{-1} mol^{-1}. The empirical correlation in eq 8 leads to $\Delta_{\text{sub}}C^{\text{o}}_{\text{p,m}} = -(29.8 \pm 33.0)$ J K^{-1} mol^{-1}. Thus, using the average of the two $\Delta_{\text{sub}}C^{\text{o}}_{\text{p,m}}$ values indicated above, $\Delta_{\text{sub}}H^{\text{o}}_{\text{m}}$(**2**,298.15 K) = 83.2 kJ mol^{-1} is derived. Although we failed to obtain clean sublimations in several other runs, this experimental result supports our previously estimated value of the enthalpy of sublimation of pyracylene.[45] This estimate, $\Delta_{\text{sub}}H^{\text{o}}_{\text{m}}$(**2**) = 84.9 ± 5.0 kJ mol^{-1},[45] was therefore accepted in the present paper and used to derive $\Delta_{\text{f}}H^{\text{o}}_{\text{m}}$(**2**,g) = 410.3 ± 5.6 kJ mol^{-1} from $\Delta_{\text{f}}H^{\text{o}}_{\text{m}}$(**2**,cr) = 325.4 ± 2.5 kJ mol^{-1} (Table 1).

The results of the three series of calorimetric studies of the hydrogenation of pyracylene in toluene at 298.15 K, using different pyracylene/styrene molar ratios, *r*, were as follows: $r = 0.4733$, $\Delta_{\text{hyd}}H^{\text{o}}_{\text{m}}$(**2**) = −(254.0 ± 9.1) kJ mol^{-1}; $r = 0.4831$, $\Delta_{\text{hyd}}H^{\text{o}}_{\text{m}}$(**2**) = −(242.3 ± 10.5) kJ mol^{-1}; $r = 0.4812$, $\Delta_{\text{hyd}}H^{\text{o}}_{\text{m}}$(**2**) = −(250.6 ± 6.2) kJ mol^{-1}. The uncertainties represent twice the standard deviation of the mean of nine runs, where pyracylene and styrene were alternately injected in the calorimetric vessel (a total of 18 hydrogenations each). The weighted mean of the above three results is $\Delta_{\text{hyd}}H^{\text{o}}_{\text{m}}$(**2**) = −(249.9 ± 4.6) kJ mol^{-1} (Table 1). The corresponding value in the gas phase, calculated from the enthalpies of formation of gaseous pyracene and pyracylene obtained in this work, is $\Delta_{\text{hyd}}H^{\text{o}}_{\text{m}}$(**2**) = −(236.0 ± 7.7) kJ mol^{-1} (Table 1). Only minor discrepancies are observed when this value is compared with the corresponding enthalpies of hydrogenation in toluene, indicated above within their combined uncertainty intervals. The difference between the enthalpies of hydrogenation of acenaphthylene in solution and in the gas phase is also small: $\Delta_{\text{hyd}}H^{\text{o}}_{\text{m}}$(**1**,g) − $\Delta_{\text{hyd}}H^{\text{o}}_{\text{m}}$(**1**,sln) = 6.6 ± 5.9 kJ mol^{-1}.

The enthalpies of formation of **1**, **2**, **3**, **4**, benzene (**6**), and naphthalene (**7**), calculated by the MM3 method, are compared in Table 2 with the corresponding experimental values. The calculated structures of **1**−**4** are planar. A conformational search yielded no conformers within 14.6 kJ mol^{-1} of the ground state. The energy cutoff of 14.6 kJ mol^{-1} was arbitrarily selected as an energy above which no significant contribution would be made to the conformational mixture. A Boltzmann distribution calculation showed that a conformer 14.6 kJ mol^{-1} above the ground state would make a contribution of less than 0.3% to

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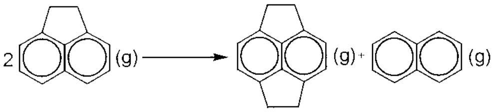
Table 2. Comparison between the Enthalpies of Formation and Hydrogenation at 298.15 K Computed by Molecular Mechanics and DFT, and the Corresponding Experimental Values (Strain Energies are Indicated in Parentheses)

	$\Delta_f H^o_m$(g)/kJ mol^{-1}			$-\Delta_{hyd} H^o_m$/kJ mol^{-1}		
compound	MM3[a]	DFT[b]	experimental	MM3[a]	DFT[b]	experimental
benzene (**6**)	84.9 (0.0)		82.6 ± 0.7[c]			
naphthalene (**7**)	150.2 (0.0)		150.3 ± 1.4[c]			
acenaphthylene (**1**)	268.2 (51.5)		263.8 ± 3.4[d]	110.9		
						107.9 ± 4.2[e]
						114.5 ± 4.2[f]
acenaphthene (**3**)	157.3 (28.0)		155.9 ± 2.5[d]			
pyracylene (**2**)	437.6 (146.4)	437.2 ± 6.9	410.3 ± 5.6[d]	249.3	244.6 ± 8.9	236.0 ± 7.0[e]
						249.9 ± 4.6[f]
pyracene (**4**)	188.3 (77.8)	192.6 ± 5.6	174.3 ± 5.3[d]			

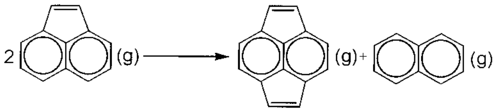
[a] Reference 36. [b] Obtained by combining the calculated reaction enthalpies [6-311+G(3df,2p)] of the isodesmic reactions 9 or 10 with the experimental enthalpies of formation of naphthalene and **3** or **1** (see text). [c] Reference 23. [d] This work. [e] This work, gas phase. [f] This work, toluene solution.

the mixture, that is, a contribution of <0.4 kJ mol^{-1} to the enthalpy of hydrogenation at 298.15 K. The MM3 results in Table 2 lead to $\Delta_{hyd}H^o_m(\mathbf{1},g) = -110.9$ kJ mol^{-1} and $\Delta_{hyd}H^o_m(\mathbf{2},g) = -249.3$ kJ mol^{-1}.

The enthalpies of formation of **2** and **4** were also derived from density functional theory calculations of the enthalpies of the isodesmic reactions shown in eqs 9 and 10. The calculated reaction enthalpies are quite insensitive to the basis set as well as to zero-point and thermal energy corrections: 30.7 [6-31G-(d)], 30.6 [6-311+G(2d,p)], and 31.1 kJ mol^{-1} [6-311+G(3df,-2p)] for eq 9, and 59.2, 59.1, and 59.9 kJ mol^{-1} for eq 10. Combining the calculated $\Delta_r H^o_m$ [6-311+G(3df,2p)] with the experimental enthalpies of formation of **1**, **3**, and **7**, given in Table 2, we obtain $\Delta_f H^o_m(\mathbf{2},g) = 437.2 \pm 6.9$ kJ mol^{-1} and $\Delta_f H^o_m(\mathbf{4},g) = 192.6 \pm 5.6$ kJ mol^{-1} at 298.15 K, leading to $\Delta_{hyd}H^o_m(\mathbf{2},g) = -(244.6 \pm 8.9)$ kJ mol^{-1} (the uncertainties include only the standard errors of the experimental values used). These DFT results are compared in Table 2 with the corresponding MM3 and experimental values.



(9)



(10)

The comparison between the calculated and experimental $\Delta_f H^o_m$(g) data in Table 2 shows that the MM3 method leads to discrepancies of 27.3 kJ mol^{-1} (pyracylene) and 14.0 kJ mol^{-1} (pyracene) and the DFT method to 26.9 kJ mol^{-1} (pyracylene) and 18.3 kJ mol^{-1} (pyracene).

The agreement between the MM3, DFT, and experimental results is satisfactory for the hydrogenation enthalpies of acenaphthylene and pyracylene. In the case of acenaphthylene, the MM3 method gives $\Delta_{hyd}H^o_m(\mathbf{1},g) = -110.9$ kJ mol^{-1}, in excellent agreement with the corresponding experimental value $\Delta_{hyd}H^o_m(\mathbf{1},g) = -(107.9 \pm 4.2)$ kJ mol^{-1}. The experimental enthalpy of hydrogenation of pyracylene, $-(236.0 \pm 7.0)$ kJ mol^{-1}, agrees with the DFT prediction, $\Delta_{hyd}H^o_m(\mathbf{2},g) = -(244.6 \pm 8.9)$ kJ mol^{-1}, within the combined uncertainties and shows a difference of 13.3 kJ mol^{-1} when compared with the MM3 result, $\Delta_{hyd}H^o_m(\mathbf{2},g) = -249.3$ kJ mol^{-1}. This difference is within the expected accuracy of the MM3 method for this type of systems, particularly when the uncertainty of the experimental value is considered.[59]

It is interesting to note that both the experimental and the computed (MM3 and DFT) enthalpies for reactions 9 and 10 are not consistent with the assumption of group additivity. According to the group additivity principle, these reactions should be thermoneutral. From the data in Tables 1 and 2, one obtains $\Delta_r H^o_m(9) = 23.9$ (MM3), 31.1 (DFT), and 12.8 ± 7.4 kJ mol^{-1} (experimental) and $\Delta_r H^o_m(10) = 51.4$ (MM3), 59.9 (DFT), and 33.0 ± 8.9 kJ mol^{-1} (experimental). Reaction 10 is also predicted to be endothermic by ab initio calculations at the 6-31G* SCF and the RMP2 levels of theory, which give $\Delta_r H^o_m(10) = 63.2$ kJ mol^{-1} and $\Delta_r H^o_m(10) = 61.5$ kJ mol^{-1}, respectively.[60]

The self-consistent field part of the MM3 calculations requires specification of the type of π carbon atoms in the molecule. The results in Table 2 were obtained assuming that one and two etheno bridges were bonded to the naphthalenic systems of acenaphthylene and pyracylene, respectively. The agreement between the calculated and experimental enthalpies of hydrogenation of acenaphthylene and pyracylene in Table 2 supports the MM3 calculations for hydrogenation of one and two etheno double bonds in acenaphthylene and pyracylene, respectively, but not of the naphthalene or any of the bonds therein. The results therefore suggest that, on energetic grounds, no significant aromatic interaction between the etheno bridges and the naphthalenic moiety of compounds **1** and **2** exists, thus favoring structure **1a** for acenaphthylene and **2a** for pyracylene.

Finally, the results in the present paper enable us to compare the aromaticity/antiaromaticity of naphthalene, acenaphthylene, and pyracylene in terms of the homodesmotic stabilization enthalpy criterion.[2,61] The homodesmotic stabilization enthalpies (HSE) of naphthalene, acenaphthylene, and pyracylene correspond to the enthalpies of reactions 11−13. Using $\Delta_f H^o_m(C_2H_4,g) = 52.5 \pm 0.3$ kJ mol^{-1},[23] $\Delta_f H^o_m(C_4H_6,g) = 110.0 \pm 1.0$ kJ mol^{-1},[23] and the experimental values of $\Delta_f H^o_m(\mathbf{1},g)$ and $\Delta_f H^o_m(\mathbf{2},g)$ in Table 1, it is concluded that $\Delta_r H^o_m(11) = 142.2 \pm 6.5$ kJ mol^{-1}, $\Delta_r H^o_m(12) = 91.2 \pm 9.2$ kJ mol^{-1}, and $\Delta_r H^o_m(13) = 7.2 \pm 12.1$ kJ mol^{-1}. Note that $\Delta_r H^o_m(13) = -20.1$ kJ mol^{-1} or $-(19.7 \pm 12.8)$ kJ mol^{-1}

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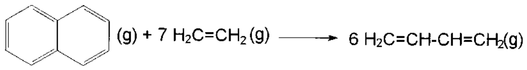
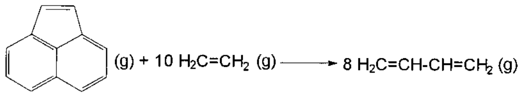
(60) Schulman, J. M.; Disch, R. L. *J. Mol. Struct.* (*THEOCHEM*) **1992**, *259*, 173−179.

(61) Glukhovtsev, M. *J. Chem. Educ.* **1997**, *74*, 132−136.

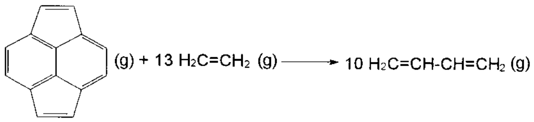
would be obtained if the $\Delta_f H^o_m(\mathbf{2},g)$ computed by the MM3 or DFT methods (Table 2), respectively, was used in the calculation.



$$(g) + 7\ H_2C{=}CH_2(g) \longrightarrow 6\ H_2C{=}CH{-}CH{=}CH_2(g) \qquad (11)$$



$$(g) + 10\ H_2C{=}CH_2\ (g) \longrightarrow 8\ H_2C{=}CH{-}CH{=}CH_2\ (g) \qquad (12)$$



$$(g) + 13\ H_2C{=}CH_2\ (g) \longrightarrow 10\ H_2C{=}CH{-}CH{=}CH_2\ (g) \qquad (13)$$

According to the homodesmotic stabilization enthalpy criterion, an [*n*]annulene is assigned as aromatic if its HSE is positive and antiaromatic if its HSE is negative.[2] The enthalpies of reactions 11−13 indicate that naphthalene and acenaphthylene are clearly aromatic, while, within the error of the experimental determinations, pyracylene may be marginally aromatic or antiaromatic. The calculation of the enthalpy of reaction 13 based on $\Delta_f H^o_m(\mathbf{2},g)$ obtained by the MM3 or DFT methods points to a small antiaromatic character of pyracylene. Thus, although the energetic criterion favors model **2a** and the magnetic criterion favors model **2b** for pyracylene, both suggest that pyracylene may be a borderline case of aromatic/antiaromatic character (recall that, as mentioned in the Introduction, only a moderate paratropic shift is observed in the ^{1}H NMR spectrum of pyracylene relative to other [4*n*]annulenes). The aromaticity trend naphthalene > acenaphthylene > pyracylene obtained by the HSE criteria may be viewed as resulting from the bonding of strongly localized 2-π-electron etheno systems to the 10-π-electron aromatic naphthalene unit.

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Supporting Information Available: Tables with the results of all individual combustion experiments carried out on acenaphthylene, acenaphthene, pyracylene, and pyracene; auxiliary data used in the correction of the energy of the isothermal bomb process to the standard state; vapor pressures of pyracene as a function of the temperature; and total energies, zero-point energies, and thermal corrections (hartrees) and enthalpies of formation (kJ mol^{-1}) of naphthalene, acenaphthylene, pyracylene, acenaphthene, and pyracene from DFT calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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