

The Enthalpy of Formation of Pyracylene

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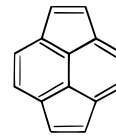
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Pyracylene **1** is a key compound in the context of aromaticity concepts and as a substructure of the fullerenes.^{1,2} The published enthalpies of formation of pyracylene in the gaseous state obtained by various theoretical methods^{3–6} span a range of ca. 100 kJ·mol⁻¹. Such discrepancies call for an experimentally determined value of $\Delta_f H_m^\circ(\mathbf{1}, \text{g}, 298 \text{ K})$. Until recently, however, it was impossible to produce a solid sample of **1** suitable for combustion calorimetry.³ The compound was first prepared in solution, about 20 years ago, by Trost and co-workers, in their search for experimental evidence of the antiaromatic character of cyclic $4n$ systems.⁷ The attempts to isolate **1** in the solid state by these authors always produced amorphous polymers.^{7a} This apparent instability of **1** in the solid state was in line with the proposed antiaromatic character of the molecule⁷ and also, for example, with the results of Aihara and Hosoya, who calculated the resonance energy for a considerable number of polycyclic unsaturated hydrocarbons (PUHs) and concluded that **1** was by far the least stable of the compounds studied.⁸ These results led to the general idea that **1** was a very unstable compound that could not be isolated in the solid state.⁹ It was recently found, however, that **1** could be isolated in the solid state from the pyrolysis of pyrene quinones, and stored for several

days at room temperature or for years at -20°C without decomposition.³

Herein we report the first experimental determination of the enthalpy of formation of **1** in the crystalline state



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and propose what we believe to be a reliable value for $\Delta_f H_m^\circ(\mathbf{1}, \text{g}, 298 \text{ K})$. This value is compared to the predictions of various theoretical methods.

Experimental Section

The pyracylene sample used in this work was prepared and purified as described previously.³ A final purification by sublimation at $65\text{--}70^\circ \text{C}$ and 10^{-3} Torr gave **1**, which was free of impurities as judged by ¹H NMR and UV–vis spectroscopy.

The standard energy of combustion of **1** was measured using a microcombustion calorimeter.¹⁰ This apparatus has been successfully used before, e.g., for C₆₀.¹¹ In a typical calorimetric experiment, a pellet of **1** was placed in a platinum crucible containing *n*-hexadecane (B.D.H., used as combustion aid) and burned under 30 atm of oxygen (ArLíquido N45, mass fraction > 0.9995) with 50 μL of water inside the stainless steel bomb of 17.95 cm³ internal volume. The HNO₃ formed from traces of atmospheric N₂ inside the bomb was determined as NO₃⁻, using a Dionex 4000i ion chromatography apparatus.

Results and Discussion

The auxiliary data needed to calculate the mass of the sample from its apparent mass in air and to calculate the standard states correction¹² are as follows. For *n*-hexadecane: $\Delta_c u^\circ = -(47150.10 \pm 1.33) \text{ J}\cdot\text{g}^{-1}$,¹¹ density = $0.773 \text{ g}\cdot\text{cm}^{-3}$,¹³ specific heat capacity = $2.216 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$,¹³ and $-(\partial u/\partial p)_T = 0.0352 \text{ J}\cdot\text{atm}^{-1}\cdot\text{g}^{-1}$.¹⁴ For **1**: density = $1.307 \text{ g}\cdot\text{cm}^{-3}$,³ specific heat capacity = $1.10 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$,¹⁵ and $-(\partial u/\partial p)_T = 0.012 \text{ J}\cdot\text{atm}^{-1}\cdot\text{g}^{-1}$.¹⁶ The energy equivalent of the calorimeter and its standard deviation, $\epsilon(\text{calor}) = 1809.67 \pm 0.36 \text{ J}\cdot\text{K}^{-1}$, had been previously determined from the combustion of benzoic acid (B.D.H.), whose energy of combustion under certificate conditions was $-(26433 \pm 2) \text{ J}\cdot\text{g}^{-1}$.

(9) In the latest edition of the widely used textbook by March (March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley: New York, 1992, p 65), pyracylene is referred to as an unstable compound impossible to isolate in the solid state, and its instability is attributed to the strain in the molecule. Interestingly, a thermodynamic study of the stability of PUHs in the gas phase at high temperatures (ref 4) suggests that pyracylene is the most stable hydrocarbon of composition C₁₄H₈ in the range 1500–3000 K.

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(15) The specific heat capacity of pyracylene at 298.15 K was measured in this work using a DSC 7 from Perkin-Elmer.

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(2) See, for example: (a) *The Fullerenes, New Horizons for the Chemistry Physics and Astrophysics of Carbon*; Kroto, H. W., Walton, D. R. M., Eds.; Cambridge University Press: Cambridge, 1993. (b) *The Fullerenes*; Kroto, H. W., Fischer, J. E., Cox, D. E., Eds.; Pergamon: Oxford, 1993. (c) *Buckminsterfullerenes*; Billups, W. E., Ciufolini, M. A., Eds.; VCH: New York, 1993. (d) Sokolov, V. I. *Russ. Chem. Bull.* **1993**, *42*, 1. (e) Matsuzawa, N.; Ata, M.; Dixon, D. A.; Fitzgerald, G. J. *Phys. Chem.* **1994**, *98*, 2555. (f) Warner, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 11059. (g) Yoshida, M.; Osawa, E. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2083. (h) Solà, M.; Mestres, J.; Duran, M. *J. Phys. Chem.* **1995**, *99*, 10752.

(3) (a) Freiermuth, B.; Gerber, S.; Riesen, A.; Wirz, J.; Zehnder, M. *J. Am. Chem. Soc.* **1990**, *112*, 738. (b) The effect of the purification steps described in ref 3a was tested in that work by analytical GC (Hewlett-Packard 8500, methyl–5% phenyl silicone column, 12 m long and 0.35 mm internal diameter) and by HPLC (reversed-phase column Merck LiChrosorb RB-8; eluent 60% acetonitrile–40% water). The only impurity detected after the chromatography step (Alumina/AgNO₃) was a small amount of 1,2-dihydropyracylene (<1%). The latter can be easily and sensitively detected by its structured UV absorption in the absorption window of pyracylene [270–320 nm, smooth absorbance background $\log(\epsilon/\text{cm}^{-1} \text{ mol}^{-1}) = 3.0\text{--}3.5$].

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Table 1. Results of the Combustion Experiments on Pyraclyene (1)^a

$m(\mathbf{1})/\text{mg}$	9.4452	16.0670	20.6345	17.0216	17.2085
$m(\text{C}_{16}\text{H}_{34})/\text{mg}$	2.3812	4.4741	1.9480	1.8438	1.8957
$n(\text{HNO}_3) \times 10^6/\text{mol}$	2.01	2.18	5.20	1.50	2.46
$\epsilon^i/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	0.857	0.869	0.868	0.864	0.864
$\epsilon^f/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	0.876	0.903	0.899	0.891	0.891
T_i/K	297.680 96	297.790 69	297.694 11	297.667 66	297.696 65
T_f/K	298.286 26	298.418 05	298.368 44	298.278 86	298.306 67
$\Delta T_c/\text{K}$	0.185 73	0.158 51	0.171 35	0.189 92	0.183 31
$\Delta T_{ad}/\text{K}$	0.269 57	0.468 85	0.502 98	0.421 29	0.426 72
$\Delta U_{\text{IBP}}/\text{J}$	-488.06	-848.09	-910.67	-762.76	-772.59
$\Delta U_{\text{ign}}/\text{J}$	1.76	1.76	1.76	1.76	1.76
$\Delta U(\text{HNO}_3)/\text{J}$	0.12	0.13	0.31	0.09	0.15
$\Delta U_s/\text{J}$	0.24	0.43	0.52	0.42	0.42
$\Delta U(\text{C}_{16}\text{H}_{34})/\text{J}$	-112.28	-210.96	-91.85	-86.94	-89.38
$\Delta U(\mathbf{1})/\text{J}$	-373.66	-635.59	-816.23	-673.55	-680.88
$\Delta_c u^\circ(\mathbf{1})/\text{J}\cdot\text{g}^{-1}$	-39 560.84	-39 558.72	-39556.57	-39 570.31	-39 566.49

^a ϵ^i and ϵ^f represent the energy equivalent of the system in the initial and final states, T_i and T_f are the initial and final temperatures, ΔT_c is the correction to the temperature rise, ΔT_{ad} is the adiabatic temperature rise, ΔU_{IBP} is the energy change of the internal bomb process, ΔU_{ign} is the energy change associated to the ignition of the sample, $\Delta U(\text{HNO}_3)$ is the energy change associated to the formation of nitric acid, ΔU_s represents the standard states correction, $\Delta U(\text{C}_{16}\text{H}_{34})$ and $\Delta U(\mathbf{1})$ are the contributions of *n*-hexadecane and pyraclyene, respectively, toward the total energy change, and $\Delta_c u^\circ(\mathbf{1})$ is the standard massic energy of combustion of pyraclyene.

The results of the individual combustion experiments on **1** are listed in Table 1. The mean value of the standard massic energies of combustion of **1** in Table 1 is $\Delta_c u^\circ(\mathbf{1}) = -(39562.59 \pm 2.54) \text{ J}\cdot\text{g}^{-1}$, which corresponds to $\Delta_c U_m^\circ(\mathbf{1}) = -(6971.6 \pm 3.1) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_c U_m^\circ(\mathbf{1}) = -(6971.6 \pm 3.1) \text{ kJ}\cdot\text{mol}^{-1}$. These values refer to the reaction in eq 1, at 298.15 K. The uncertainties in $\Delta_c U_m^\circ$



(**1**) and $\Delta_c H_m^\circ(\mathbf{1})$ include the contributions from the calibration and the energy of combustion of *n*-hexadecane.¹⁷ Using $\Delta_f H_m^\circ(\text{CO}_2, \text{g}) = -(393.51 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$ ¹⁸ and $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) = -(285.830 \pm 0.040) \text{ kJ}\cdot\text{mol}^{-1}$,¹⁸ then $\Delta_f H_m^\circ(\mathbf{1}, \text{cr}, 298 \text{ K}) = 324.1 \pm 3.6 \text{ kJ}\cdot\text{mol}^{-1}$ is obtained.

An attempt was made to determine the enthalpy of sublimation of **1** using a method based on the measurement of the absorbance of a vapor in equilibrium with its solid as a function of the temperature.¹⁹ After the vapor was monitored for 2 days in the temperature range 323–398 K it was found that solid pyraclyene had decomposed inside the cell and the results of the experi-

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(20) The Morawetz method (Morawetz, E. *J. Chem. Thermodyn.* **1972**, *4*, 461), gives $\Delta_{\text{cr}}^{\text{g}} H_m^\circ(\mathbf{1}, 298 \text{ K}) = 81.1 \text{ kJ}\cdot\text{mol}^{-1}$. The method proposed by Gavezzotti and Desiraju (Gavezzotti, A.; Desiraju, G. R. *Acta Crystallogr.* **1988**, *B44*, 427) leads to $\Delta_{\text{cr}}^{\text{g}} H_m^\circ(\mathbf{1}, 298 \text{ K}) = 88.6 \text{ kJ}\cdot\text{mol}^{-1}$. The reliability of the two estimation methods was tested using the experimental data in the compilation by Pedley (Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; TRC Data Series: College Station, TX, 1994; Vol. I) for the following series of compounds: benzene, naphthalene, azulene, biphenylene, acenaphthylene, anthracene, pyrene, and fluoranthene. The mean values of the differences $|\Delta_{\text{cr}}^{\text{g}} H_m^\circ(\text{experimental}) - \Delta_{\text{cr}}^{\text{g}} H_m^\circ(\text{estimated})|$ found for the Morawetz method and the method of Gavezzotti and Desiraju are 1.7 and 4.7 $\text{kJ}\cdot\text{mol}^{-1}$, respectively (the corresponding maximum deviations are 5 and 7 $\text{kJ}\cdot\text{mol}^{-1}$). The average of the two estimates referred to above, $\Delta_{\text{cr}}^{\text{g}} H_m^\circ(\mathbf{1}, 298 \text{ K}) = 84.9 \pm 5.0 \text{ kJ}\cdot\text{mol}^{-1}$, was selected in this paper. The uncertainty quoted ($\pm 5.0 \text{ kJ}\cdot\text{mol}^{-1}$) was chosen to be an upper limit of the mean deviations indicated above (1.7 and 4.7 $\text{kJ}\cdot\text{mol}^{-1}$).

Table 2. Comparison between Experimental and Theoretical Results for the Enthalpy of Formation of Pyraclyene (1) in the Gaseous State (Data in $\text{kJ}\cdot\text{mol}^{-1}$)

$\Delta_f H_m^\circ(\mathbf{1}, \text{g})$	method
409.0 ± 6.2^a	experimental
366 ^b	group additivity
369 ^c	group additivity
410 ^d	MMP2
431 ^e	6-31G*(RMP2-FC)//6-31G*
433 ^e	6-31G*(SCF)
461 ^d	MNDO
503 ^f	PM3

^a This work. ^b Reference 4. ^c Reference 6. ^d Reference 3. ^e Reference 5. ^f Obtained in this work using the AMPAC/MOPAC version 6.0 with the PM3 Hamiltonian.

ment had to be discarded. The value of the enthalpy of sublimation of **1**, $\Delta_{\text{cr}}^{\text{g}} H_m^\circ(\mathbf{1}, 298 \text{ K}) = 84.9 \pm 5.0 \text{ kJ}\cdot\text{mol}^{-1}$ was, therefore, estimated using the methods proposed by Morawetz and by Gavezzotti and Desiraju.²⁰ This value and the enthalpy of formation of **1** in the crystalline state given above lead to $\Delta_f H_m^\circ(\mathbf{1}, \text{g}, 298 \text{ K}) = 409.0 \pm 6.2 \text{ kJ}\cdot\text{mol}^{-1}$ which is compared in Table 2 with the results obtained by various theoretical methods. The MM2 molecular mechanics method, which also provides accurate calculations of the bond lengths of **1**,³ predicts $\Delta_f H_m^\circ(\mathbf{1}, \text{g}, 298 \text{ K}) = 410 \text{ kJ}\cdot\text{mol}^{-1}$. This result is in excellent agreement with the value proposed in this paper. *Ab initio* 6-31G* molecular orbital calculations (which lead to more accurate predictions of the bond lengths of **1** than the MM2 method)⁵ and MNDO³ and PM3 semiempirical methods give values that are substantially in excess of the value proposed in this paper. On the other hand, the group additivity schemes of Stein and Fahr⁴ and of Moiseeva and Dorofeeva⁶ lead to $\Delta_f H_m^\circ(\mathbf{1}, \text{g}, 298 \text{ K})$ values that are much lower than the result obtained here.

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