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Experimental Enthalpies of Formation and Strain Energies for the Caged $C_{20}H_{20}$ Pagodane and Dodecahedrane Frameworks

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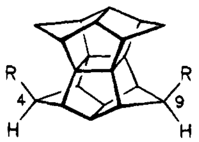
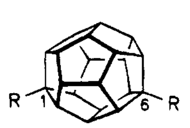
Abstract: The enthalpies of formation ($\Delta H_f^\circ(g)$) and the strain energies (E_{str}) have been determined from combustion calorimetry for [1.1.1.1]pagodane **1** (47.9; 95.5 kcal/mol), its 4,9-bis(methoxycarbonyl) derivative **3** (−107.3; 95.5 kcal/mol) and the 1,6-bis(methoxycarbonyl)dodecahedrane **4** (−151.8; 61.4 kcal/mol). On the basis of these measurements $\Delta H_f^\circ(g) = 22.4 \pm 1$ kcal/mol (standard deviation) and $E_{str} = 61.4 \pm 1$ kcal/mol are reliable estimates for parent $(CH)_{20}$ dodecahedrane **2**, an "evergreen" for computational activities, in good agreement with the MM2 predictions.

Introduction

The $C_{20}H_{20}$ hydrocarbons [1.1.1.1]pagodane **1**[1] and pentagonal dodecahedrane **2**[2,3] are the parent representatives of two prominent families of organic cage compounds. For the design of synthetic strategies to be followed within the pagodane−dodecahedrane scheme,[4,5] particularly for the evaluation of the various routes developed for the installation of functionalities into **1** and **2**,[6,7] and for the assessment of energetic and steric differences within related sets of cage structures, force-field calculations (MM2, MM3)[8−11] have proven to be highly serviceable. The appreciable level of reliability achieved with respect to structural parameters was attested to by X-ray structural analyses for most of the molecular frameworks in question (pagodanes,[1,12] bissecododecahedranes,[13,14] secododecahedranes,[15,16] dodecahedranes[17−21]). However, whenever it came to absolute energies, larger errors in the force-field data had to be anticipated.[8−11] Semiempirical and *ab initio* calculations—whilst generally confirming the energetic trends manifested in the force-field data—furnished rather conflicting results. The enthalpies of formation ($\Delta H_f^\circ(g)$) and strain



1 (R=H)
3 ($R=CO_2CH_3$)



2 (R=H)
4 ($R=CO_2CH_3$)

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Table 1. Theoretical $\Delta H_f°$ and $E_{str}{}^a$ Data for **1** and **2** (kcal/mol)

		1			**2**		
		$\Delta H_f°$	$E_{str}{}^a$	ref	$\Delta H_f°$	$E_{str}{}^a$	ref
MM1	(1971)				45.3	88.5	23
EAS	(1973)				−0.2	43.0	24
MM2	(1979)	64.4	112.0	5	22.2	65.4	25
MM3	(1992)	72.3	119.9	18	39.4	82.6	19
SSR	(1973)					(42.6)[b]	26
MINDO/3	(1978)				62.3	105.5	27
MNDO	(1984)				−46.9	−3.7	28
STO-3G	(1984)				−8.1	35.1	28
4-31G	(1984)				−3.5	39.7	28
6-31G*	(1985)				4.6		29
	(1989)				12.8	56.0	30a
EFF	(1990)				−8.4	34.8	31
MP2/6-31G*	(1994)	27.8		22			
6-31G*	(1994)	48.2[c]		30c			

[a] Strain energy was calculated from the $\Delta H_f°$ value by a common scheme (see Table 2, footnote *c*) to obtain comparable values. The authors partly used different definitions of strain energy. [b] Strain given by the authors. [c] From the calculated energy difference between **1** and **2** $\Delta\Delta H_f° = 43.6$ kcal/mol (6-31G* level)[30c] and the earlier reported $\Delta H_f°$ (**2**) = 4.6 kcal/mol from the homodesmic method at the 4-31G* level.[29]

Table 2. Experimentally Determined Heats of Combusion ($\Delta H_c°$), Heats of Sublimation (ΔH_{sub}), Standard Heats of Formation ($\Delta H_f°$(c), $\Delta H_f°$(g)), and Strain Energies (E_{str}) in kcal/mol ($\pm\sigma$) of **1**, **3**, and **4**

	1	**3**	**4**
$\Delta H_c°(c)^a$	−2590.49 ± 0.73	−2934.75 ± 0.46	−2891.89 ± 0.77
$\Delta H_{sub}{}^b$	21.56 ± 0.54	34.92 ± 0.72	33.40 ± 0.29
$\Delta H_f°$(c)	26.32 ± 0.73	−142.25 ± 0.46	−185.04 ± 0.77
$\Delta H_f°$(g)	47.88 ± 0.91	−107.33 ± 0.85	−151.80 ± 0.82
$E_{str}{}^c$	95.52	110.03	61.36

[a] Obtained from the specific heats of combustion $\Delta u°_c$ in Table 5. [b] Obtained from the temperature dependence of the vapor pressures in Table 6. [c] $E_{str} = \Delta H_f°(g) - \Delta H_f N$. The strain free reference values of the heats of formation ($\Delta H_f N$) are defined by group increments, obtained from a series of aliphatic esters[42] and from group increments for alkanes.[43]

energies (E_{str}) as derived for **1** and **2** from calculations of increasing levels of sophistication are listed in Table 1. In particular, the I_h symmetrical nature of **2** with its 20 perfectly eclipsed C−H bonds attached to a nearly strain-free carbon skeleton together with its historical connotations,[32] and its more recent consideration as perhydro-C_{20} fullerene[3b,33]—has appealed to theoreticians as a testing ground for their methodological improvements.[22−35] The excitement of submitting these predictions for **1** and **2** to experimental scrutiny has existed ever since their synthesis was accomplished,[1,2] yet was tempered particularly for **2** by the amount of time and effort needed for the acquisition of sufficient material for combustion measurements. With pagodanes and dodecahedranes now at hand in relatively large quantities,[2d,3b] the reluctance to put such valuable compounds "through the chimney" ("Who wants to burn diamonds?"[36]) has now been overcome. In this paper we report on our efforts to determine experimentally the thermochemical properties of **1** and **2** and their bis(methoxycarbonyl) derivatives **3** and **4**.

Thermochemical Measurements

The heat of combustion measurements were performed in an isoperibolic aneroid microcalorimeter.[37] This equipment has been successfully used before (e.g., fullerenes[38]). The combustion of the pellets of material was complete in all cases and no soot or carbon monoxide was formed (<0.03%); the addition of mineral oil as an auxiliary material[39] had no influence on the results obtained. The samples to be studied were purified by chromatography, recrystallization, and sublimation in vacuo. No impurity ≥0.02% could be detected[40] by GC, and no change of the samples occurred during storage under bomb conditions (30 atm O_2) for 1 day. Initially, we studied the parent hydrocarbons **1** and **2**. Whereas the results for a series of measurements with **1** were consistent, they were not consistent for several samples of **2** from either Columbus or Freiburg. A comprehensive analysis of the samples of **2** which were purified by crystallization and sublimation (purity better than 99.98%) could not establish the reason for this scatter.[40] We coped with this problem by turning toward the diesters **3** and **4**. Details of the procedures and the experimental data are listed in Tables 4−6: the standard heats of combustion, the standard heats of formation, and the strain energies of **1**, **3**, and **4** in Table 2. The enthalpies of sublimation were deduced from the temperature dependence of the vapor pressures (Clausius−Clapeyron). The latter were measured by the slow flow method developed earlier.[41]

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Table 3. $E_{str}{}^{a}$ of **1**–**4** by Molecular Mechanics (kcal/mol)

	pagodanes		dodecahedranes	
	1	**3**	**2**	**4**
MM2[b]	112.0	127.4	65.4	65.9
MM3[c]	119.9	123.8	82.6	84.1
exp.[d]	95.5	110.0		61.4
MM2-exp	16.5	17.4		4.5
MM3-exp	24.4	16.5		22.7

[a] Strain energies are calculated from $\Delta H_f°(g)$ by the usual scheme (see Table 2, footnote c) for comparison. [b] Calculated with the MM2 program ref 8. [c] Calculated with the MM3 program ref 44. [d] Standard errors of Table 2.

Table 4. Results of Typcial Combustion Experiments of **1**, **3**, and **4**[a]

	1	**3**	**4**
m (mg)	24.989	39.066	43.684
m_{fuse} (mg)	0.644	0.500	0.572
ΔT_c (K)[b]	0.74686	0.86902	0.95827
$\epsilon_{calor}\cdot\Delta T_c$ (cal)[c]	251.16	306.31	337.70
$-\epsilon_{cont}\cdot\Delta T_c$ (cal)[d]	−0.46	−0.56	−0.61
ΔE_{Korr} (cal)[e]	0.13	0.19	0.21
$m_{fuse}\ \Delta u_c$(fuse) (cal)	2.61	2.03	2.31
Δu_c (cal/g)	−9937.7	−7789.3	−7678.3

[a] Notations see ref 45; weights in vacuum; $T_h = 25$ °C; $T_f = 24.99$–25.01 °C; $V_{bomb} = 0.046$ l; $p^i_{gas} = 30.00$ atm (30.40 bar); $m^i_{H2O} = 0.23$ g; $E_{ign} = 0.55$ cal; $m_{platinium} = 2.3 - 2.6$ g. [b] $\Delta T_c = T_f - T_i + \Delta T_{korr}$. [c] $\epsilon_{calor} = 341.076 \pm 0.034$ (**1**), 352.476 ± 0.070 (**3**), and 352.409 ± 0.024 (**4**). [d] $-\epsilon_{cont}\ \Delta T_c = \epsilon^i_{cont}\ (T_i - T_h) + \epsilon^f_{cont}\ (T_h - T_f + \Delta T_{korr})$. [e] Sums of items 81–85, 87–90, 93, and 94 in ref 45.

Discussion

For pagodane **1**, the experimental $\Delta H_f°(g)$ and E_{str} values expectedly differ significantly (16.5 kcal/mol) from the MM2 predictions (and even more from those based on MM3). When the force-field calculations had been introduced at the planning stage of the project,[4,5] it was understood that the MM2 data for the pagodanes with its special structural features would be subject to a significant error. The thermochemical results ($\Delta H_f°(g)$) place pagodane-diester **3** by 44.5 kcal/mol above dodecahedrane-diester **4**. For comparing the stabilities of **1**, **3**, and **4**, the strain energy E_{str} was taken as reference in order to account for the differential contribution of the two substituents and for the different branching of the C atoms in the two isomers **3** and **4**. When calculated by the usual group increment scheme (Table 2, footnote c), E_{str} for diester **3** was found to be higher by 48.7 kcal/mol than for diester **4**. Since parent pagodane **1** turned out to be less strained than its diester **3** by 14.5 kcal/mol—primarily a manifestation of the "cavity-strain" produced in **3** by repulsion between the *syn*-positioned ester groups and the cage—ΔE_{str} for **3** and **4** (48.7 kcal/mol, Table 2) is not a direct measure for ΔE_{str} between the parent molecular frameworks but contains a substantial discrepancy in substituent-strain. The portion of strain contributed by the two ester groups was estimated by molecular mechanics calculations (Table 3). MM2 reproduces quite well the experimental E_{str} for **4** (65.9 vs 61.4 kcal/mol) and ΔE_{str} for **1** and **3** (15.4 vs 14.5 kcal/ mol) and has ΔE_{str} for parent dodecahedrane **2** and its diester **4** at 0.5 kcal/mol (MM3 1.5 kcal/mol). Thus, E_{str} for **2** can confidently be assigned as 61.4 ± 1 kcal/mol. A reliable estimate by subtracting two increments of −90.0 kcal/mol for CCO_2CH_3[42] from $\Delta H_f°(g) = -151.80 \pm 0.82$ kcal/mol for **4** and by adding two increments of −2.16 kcal/mol for CH[43] places $\Delta H_f°(g)$ for **2** at 22.4 ± 1.0 kcal/mol, clearly in good agreement with the MM2 value (the standard deviation (std) results from the experimental std of **4** and the precision of the group increment procedure[42]). Due to the above stated discrepancy of 16.5 kcal/mol relative to MM2 for $\Delta H_f°(g)$ of **1**, the exothermicity of the isomerization **1** → **2** ($\Delta\Delta H_f°(g)$) is smaller than originally assumed for the pagodane → dodecahedrane conversion[3,4] but still amounts to 25.5 kcal/mol.

Table 5. Specific Energies of Combustion (Δu_c) Calculated from All Combustion Experiments[a] (cal/g)

	1	**3**	**4**
Δu_c	−9939.0	−7790.2	−7671.7
	−9937.9	−7784.9	−7681.5
	−9927.3	−7792.1	−7678.1
	−9937.7	−7790.5	−7670.9
	−9946.9	−7789.3	−7678.3
	−9934.7		
	−9944.5		
mean value	−9938.4 ± 2.4	−7789.4 ± 1.2	−7676.1 ± 2.1

[a] For the resulting standard heats of combustion see Table 2.

Table 6. Vapor Pressure of **1**, **3**, and **4** as Measured by the Flow Method[a]

$T_{sat}{}^{a}$ (°C)	v (l h^{-1})	V (l)	$m_{sub}{}^{d}$ (mg)	p (torr)
		1[b]		
145.0	0.96	69.1	0.399	$4.12\cdot10^{-4}$
150.0	0.93	61.1	0.438	$5.12\cdot10^{-4}$
160.0	0.95	16.8	0.241	$1.02\cdot10^{-3}$
178.0	0.89	16.1	0.886	$3.93\cdot10^{-3}$
180.0	1.93	8.13	0.494	$4.34\cdot10^{-3}$
180.0	0.52	8.32	0.494	$4.24\cdot10^{-3}$
190.0	0.92	0.817	0.0948	$8.28\cdot10^{-3}$
195.0	1.00	3.00	0.480	$1.14\cdot10^{-2}$
200.0	0.98	0.975	0.208	$1.52\cdot10^{-2}$
		3[c]		
119.7	0.98	180.0	0.139	$3.82\cdot10^{-5}$
124.8	1.06	27.4	0.419	$7.55\cdot10^{-5}$
130.1	0.98	88.2	0.275	$1.54\cdot10^{-4}$
140.0	0.98	72.3	0.643	$4.39\cdot10^{-4}$
149.8	1.75	42.3	0.781	$9.12\cdot10^{-4}$
150.2	0.95	23.0	0.576	$1.24\cdot10^{-3}$
160.2	0.98	16.6	1.10	$3.27\cdot10^{-3}$
169.6	0.98	4.71	0.600	$6.29\cdot10^{-3}$
170.2	0.98	5.36	0.827	$7.61\cdot10^{-3}$
174.3	1.11	5.05	0.931	$9.10\cdot10^{-3}$
		4[d]		
121.5	0.93	62.0	0.128	$1.02\cdot10^{-4}$
131.2	0.95	22.8	0.127	$2.74\cdot10^{-4}$
132.9	0.91	68.3	0.595	$4.31\cdot10^{-4}$
152.1	0.94	16.5	0.679	$2.04\cdot10^{-3}$
161.2	0.91	4.85	0.517	$5.27\cdot10^{-3}$
176.5	0.91	2.35	0.891	$1.87\cdot10^{-2}$

[a] Saturation of V of flowing N_2 (v) and condensation of the compounds (m_{sub}) at condensation temperature T_{cond}. [b] $T_{cond} = 14$–15 °C. [c] $T_{cond} = 21$–22 °C. [d] $T_{cond} = 12$–13 °C.

Experimental Section

General Aspects. Spectroscopy: ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AM 400 using Me_4Si or $CDCl_3$ as reference. Gas chromatography: Capillary-Column-GC Vega Series GC 6000 (FID), Carlo Erba, either split injector (270 °C) or cold on column technique; 15 m column SE 30 with electronic integrator HP 3393, Hewlett-Packard.

Materials. Undecacyclo [9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane (1). The sample (ca. 0.5 g) was prepared according to ref 1, recrystallized from CH_2Cl_2/ethyl acetate, and slowly sublimed at 140 °C/14 Torr. Purity > 99.99% (VPC). **Undecacyclo [9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (2).** The sample

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(42) Rakus, K.; Keller, M.; Verevkin, S. P.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.*, manuscript in preparation. Verevkin, S. P.; Dogan, B.; Beckhaus, H.-D.; Rüchardt, C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 674. $CH_3CO_2CH = -90.0$, $CH_3CO_2C = -87.14$ kcal·mol^{-1}

(ca. 0.5 g) was prepared according to ref 3b, recrystallized from benzene and slowly sublimed at 140 °C/14 Torr. Purity > 99.85% (VPC). The sample (ca. 0.1 g) prepared according to ref 2d was very slowly recrystallized from benzene to give material of >99.9% purity (capillary GC). **Dimethyl undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-4-syn,9-syn-dicarboxylate (3).** The sample (ca. 0.5 g) was prepared according to ref 1, recrystallized from benzene, and slowly sublimed at 140 °C/14 Torr. Purity > 99.85% (VPC). **Dimethyl undecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,6-dicarboxylate (4).** The sample (ca. 0.5 g) was prepared according to ref 6b, recrystallized from CH_2Cl_2/ethyl acetate, and slowly sublimed at 140−150 °C/2 × 10^{-3} Torr (15 mg/h). At higher temperatures decomposition of **4** sets in. Purity > 99.98% (VPC).

Heats of Combustion. Samples (30−50 mg) of **1**−**4** were pressed (3 t) into tablets of 5 mm diameter. The weights (Microbalance Sartorius) have been corrected to vacuum in order to obtain the masses, using the densities d = 1.37(1), 1.20(3), and 1.24(4) determined by floating in an aqueous solution of salt of known density. The combustion experiments were performed in our aneroid isoperibolic calorimeter[37] equipped with a quartz-thermometer HP 28024, by the usual procedure.[37] Complete combustion was generally ascertained by careful inspection of the calorimetric bomb before and after burning. The isothermic bomb processes and the correction to standard states were calculated following the procedure in ref 45 (see Table 4). The specific heat capacities were measured by DSC c_p = 0.24(**1**), 0.23(**3**), and 0.21(**4**) cal/g K. Calibration experiments were performed with benzoic acid (NBS, standard reference sample 39i). The results of all experiments are listed in Table 5.

Heats of Sublimation. Finely powdered samples (ca. 0.1 g) were mixed with glass pellets (diameter ≈ 1 mm) and filled in a tube[41] which was heated to a constant temperature T_{sat}. A slow flow (0.5−2 l h^{-1}) of N_2 was drifting through this tube and through a cooled trap connected to the saturation tube. The condensed material was quantitatively analyzed by GC after adding a previously defined amount of an internal standard. The saturation pressure p at T_{sat} of the compound was calculated from these data (see Table 6 and ref 41). The linear correlation of ln p against T_{sat}^{-1} allowed the calculation of the heat of sublimation ΔH_{sub} (see Table 2).

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