Enthalpies of Formation of Hexaethylethane, Octamethylhexane, and Tri-*tert*-butylmethane. Extremely Strained Hydrocarbons[†]

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3,3,4,4-Tetraethylhexane (**1**) and 2,2,3,4,4,5,5-octamethylhexane (**2**) were synthesized from 3-ethylpentane and 2,2,3-trimethylbutane, respectively, by UV-irradiation with mercury in the gas phase. The enthalpies of combustion $\Delta H_c°$ of **1**, **2**, and tri-*tert*-butylmethane (**3**) when measured calorimetrically were $\Delta H_c°$ = −9467.2 ± 2.3, −9491.4 ± 2.3, and −8825.0 ± 4.3 kJ·mol^{-1}, respectively. The enthalpies of vaporization of **1** and **2** and the enthalpy of sublimation of **3** were derived from the temperature dependence of their vapor pressures. The latter were determined by a flow method. The resulting standard enthalpies of formation were $\Delta H_f°$ (g) = −265.5 ± 2.6, −248.3 ± 2.4, and −235.2 ± 4.3 kJ·mol^{-1} for **1**, **2**, and **3**, respectively. They correspond to strain enthalpies (H_s) of 118.1, 177.2, and 156.1 kJ·mol^{-1}, respectively. These values provide valuable test cases for semiempirical and empirical calculations.

Introduction

Sterically congested hydrocarbons[2] exhibit the important principle that steric effects increase the energy of a molecule, as measured as its heat of formation.[3] Intramolecular van der Waals repulsions are responsible for this excess energy, the so-called strain energy, which causes unique structural distortions.[2] Elongated bonds up to 165 pm[4b] are found especially between two quaternary carbon atoms[4] and enlarged bond angles (to more than 120°) at tertiary carbons.[5] The strain of branched hydrocarbons is demonstrated by their unique thermolability and by the ease of their homolytic cleavage reactions into alkyl radicals. Whereas 2,2,3,3-tetramethylbutane, often called hexamethylethane,[6] is stable up to 400 °C, 3,3,4,4-tetraethylhexane, i.e., hexaethylethane (**1**),[4a,7] has a half-life of only 1 h at 280 °C.

Although the heats of formation $\Delta H_f°$ (g) of **1** and 2,2,3,3,4,4,5,5-octamethylhexane (**2**) and, hence, their experimentally determined strain energies H_s are of general interest and should be useful as test cases for the development of calculational procedures, no measurements have been possible so far because of synthetic problems, which are common to all structures with two neighboring quaternary carbons ("C_q −C_q ethanes"[4]).

Synthesis

The best synthetic procedure[4,7] for **1** and **2**, so far, has been the dimerization of tertiary radicals R•, generated by photolysis of the corresponding azo compounds (R−N=N−R).[8] The competing disproportionation predominates, however, and causes low yields of the dimers R−R. We applied, therefore, a new method[9] that was introduced recently for the synthesis of highly strained dimers by mercury-sensitized photolysis of "monomers" RH and successfully synthesized 3,3,4,4-tetraethylhexane (**1**) and 2,2,3,3,4,4,5,5-octamethylhexane (**2**) in 22% and 16% yields, respectively. By distillation in a spinning band column a purity >99.9% was reached. A great advantage of this simple method is that the starting materials are readily accessible and cheap.

$$(C_2H_5)_3CH \xrightarrow[254\ nm]{Hg} (C_2H_5)_3C{-}C(C_2H_5)_3 \quad \mathbf{1}$$
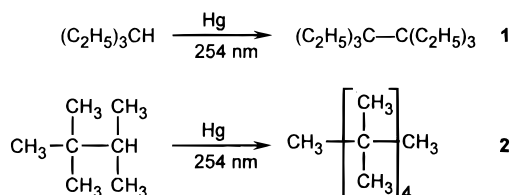
Results

The standard enthalpies of combustion $\Delta H_c°$ were measured calorimetrically.[10,11] In this context, we also

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[†] Thermolabile Hydrocarbons. 32. Part 31: see ref 1.

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Table 1.   Experimental Thermochemical Results and MM2 Calculations for Compounds 1–3 at 298 K (kJ mol^{-1})

	state	$\Delta H_c°$(l or cr)^a	$\Delta H_f°$(l or cr)	$\Delta H_{vap}°$ ^{b}	$\Delta H_f°$(g) (exptl)	$\Delta H_f°$(g) (MM2)	H_s (exp.)
1	l	-9467.2 ± 2.3	-329.4 ± 2.3	63.9 ± 1.2^c	-265.5 ± 2.6	-260.5	118.1
2	l	-9491.4 ± 2.3	-305.2 ± 2.3	56.90 ± 0.70	-248.3 ± 2.4	-253.5	177.2
3^d	cr	-8825.0 ± 4.3	-292.2 ± 4.3	57.03 ± 0.43^e	-235.2 ± 4.3	-236.0	156.1

^{a} Taken from the specific enthalpies of combustion in Table 4. ^{b} From Table 5, the mean temperatures of the measurements are about 290–310 K. ^{c} Slightly different from the preliminary result given in ref 16. ^{d} The value for the enthalpy of combustion of **3** from our previous work[12] proved to be incorrect, due to sensitivity to oxygen; the enthalpy of sublimation[12] was also in error due to the condensation of water. These interferences were eliminated by precautions mentioned in the Experimental Section. ^{e} Enthalpy of sublimation. The value of $\Delta H_{sub,7}°$ has been independently determined for **3** to be 58.6 kJ·mol^{-1} by the head-space technique.[16]

Table 2.   Purities, Densities $d_{(293K)}$, Specific Heats $c_{p(298K)}$, and Expansion Coefficients of the Materials

	purity (%)	$d_{(293K)}$^{a} (g cm^{-1})	$c_{p(298K)}$^{b} (J K^{-1} g^{-1})	$(\delta V/\delta T)$ 10^{-6} ^{c} (L g^{-1} K^{-1})
1	99.99	0.859	2.31	1.0
2	99.94	0.857	2.13	1.0
3	99.99	0.850	1.92	0.1
cotton^d		1.50	1.67	0.1
mylar^e		1.38	1.32	0.1

^{a} Measured by the suspension method. ^{b} From DSC measurements. ^{c} Estimated. ^{d} CH$_{1.774}$O$_{0.887}$, $\Delta u_c°$(cotton) $= -16\,945.2 \pm 4.2$ J g^{-1}. ^{e} C$_{10}$H$_8$O$_4$, mylar A $\Delta u_c°$(mylar) $= -22\,831.0 \pm 4.8$ J g^{-1} (combustion of **1** and **3**), mylar B $\Delta u_c°$(mylar) $= -22\,744.8 \pm 1.5$ J g^{-1} (combustion of **2**), $m_{(mylar)} = m_{moist}[1 - 4.64 \times 10^{-5}$ (relative moisture of air in %)].

reinvestigated[12] tri-*tert*-butylmethane **3** because we discovered that this compound reacts with oxygen in the calorimetric bomb at 30 atm prior to ignition. To avoid this autoxidation, the samples for combustion were prepared in a glovebox under N$_2$ and were sealed in mylar bags. For **3**, measurements in two different calorimeters gave identical results.

The enthalpies of vaporization $\Delta H_{vap}°$ of **1** and **2** and $\Delta H_{sub}°$ for **3** were obtained from the temperature dependence of the vapor pressures measured in a flow system.[13,14] These thermochemical data constitute the experimental basis for the quantitative estimation of the strain enthalpies H_s of **1–3**. They are derived as a difference between the experimental $\Delta H_f°$ (g) and the sum of strain-free increments for alkanes.[15]

A summary of the results from these measurements is given in Table 1. The given standard deviations of the mean include the uncertainties from calibration and the uncertainties from the combustion energies of the auxiliary materials.

Discussion

The strain enthalpies H_s, which are due to steric repulsion between the bulky alkyl groups, are derived from the difference between the experimental standard enthalpies of formation $\Delta H_f°$ (g) of the molecules **1–3** and the sum of the appropriate strain-free increments[15] (CH$_3$-[C] $= -42.05$, CH$_2$[2C] $= -21.46$, CH[3C] $= -9.04$ and C[4C] $= -1.26$ kJ·mol^{-1}). They are listed in Table 1. The most strained compound in this series is octamethylhexane (**2**) with the strain $H_s = 172.0$ kJ·mol^{-1}. Less strained are tri-*tert*-butylmethane **3** ($H_s = 155.2$ kJ·mol^{-1}) and hexaethylethane (**1**) ($H_s = 123.1$ kJ·mol^{-1}). In spite of this high strain, the enthalpies of formation $\Delta H_f°$ (g) of **1–3** were well reproduced (within 4–5 kJ·mol^{-1}, see Table 1) by MM2 force-field calculations.[17] The specific structural features of the symmetrically hexaalkylated ethanes **1** and **2** have been described in an earlier paper.[18] It has been shown that a strong interplay between the six geminal and vicinal alkyl groups, which may be called dynamic gearing, determines the symmetry of the structures, and often the anti conformation becomes less stable than the gauche one. **1** adopts C_2 symmetry with two ethyl groups at each C$_q$ atom in the anti-conformation and the other in the gauche-conformation. The conformation at the central C$_q$–C$_q$ bond of **1** is defined by the two gauche ethyl groups in the gauche position to each other. **2** adopts a preferred conformation with *tert*-butyl groups in the anti position (for a detailed description see ref 18). These strong steric interactions of alkyl groups, mainly intramolecular van der Waals repulsions, serve as a valuable test case for other calculational procedures.

Experimental Section

General Methods. The analytical instruments used had been described in a previous publication.[1]

Materials. Synthesis and Purification. The best synthesis for the highly strained molecules **1** and **2** is to dimerize 3-ethylpentane[16] and 2,2,3-trimethylbutane,[19] respectively, by the mercury-photosensitized dehydrodimerization.[9] The experiments were carried out in a cylindrical 1 L quartz vessel with an attached condenser. At the bottom of the vessel was attached a small Pyrex flask by a ground joint containing about 30–50 mL of the liquid monomer and, in addition, a drop of mercury. The substrate was refluxed, and simultaneously the vapor phase was irradiated (254 nm). The reaction was controlled by following the generation of hydrogen in a gas burette, which was attached to the condenser. The temperature of the condenser was kept at −30 °C to avoid the transfer of material in the gas stream.

3-Ethylpentane and 2,2,3-trimethylbutane were synthesized following the literature procedure.[19]

3-Ethylpentane:[19] ^{1}H-NMR (250 MHz, CDCl$_3$, TMS) δ 0.81 (t, 9H, CH$_3$), 1.08 (sept, 1H, (CH$_3$CH$_2$) $_3$CH), 1.26 (q, 6H, (CH$_3$CH_2CH); bp 92 °C.

2,2,3-Trimethylbutane:[19] ^{1}H-NMR (250 MHz, CDCl$_3$, TMS) δ 0.83 (d, 6H, (CH$_3$)$_2$CH), 0.84 (s, 9H, C(CH$_3$)$_3$), 1.35 (sept, 1H, C(CH$_3$)$_2$CH); bp 80 °C.

3,3,4,4-Tetraethylhexane (1). Twenty-five g of 3-ethylpentane was irradiated under reflux for 8 d (generation of 2.4 L of hydrogen) and purified by distillation of the residue: 5.5 g (22%) of **1**; ^{1}H-NMR (250 MHz, CDCl$_3$, TMS) δ 0.90 (t, 18H, 6 CH$_2$CH_3), 1.49 (q, 12H, 6 CH_2CH$_3$); ^{13}C-NMR (20 MHz,

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Table 3. Results from Typical Combustion Experiments[a]

	1	2	3 (in macro)	3 (in micro)
m(substance)[b] (g)	0.255 518	0.163 372	0.224 001	0.033 593
$m'_{(cotton)}$[b] (g)	0.000 685	0.000 677	0.000 700	0.000 800
$m''_{(mylar)}$[b] (g)	0.022 664	0.021 372	0.033 007	0.008 769
$\Delta T_c{}^c$ (K)	0.506 26	0.330 88	0.457 22	1.295 42
$\epsilon_{calor}(-\Delta T_c){}^c$ (J)	−12 701.41	−8301.31	−11 471.11	−1818.58
$\epsilon_{cont}(-\Delta T_c)$ (J)	−6.61	−4.23	−5.86	−3.51
$\Delta E_{corr.}{}^d$ (J)	3.22	1.46	3.18	2.13
$-m'\Delta u'_c{}^d$ (J)	11.67	11.46	11.88	13.56
$-m''\Delta u''_c{}^d$ (J)	517.44	488.1	755.42	200.29
$\Delta u_{c(substance)}$ (J g^{-1})	−47 645.3	−47 758.27	−47 794.67	−47 812.66
$\Delta H^\circ_{c(substance)}$ (kJ mol^{-1})	−9470.48	−9492.87	−8828.49	−8831.80
$\Delta H^\circ_{f(substance)}$ (kJ mol^{-1})	−326.10	−303.67	−288.78	−285.43

[a] For the definition of the symbols see ref 11. Macrocalorimeter: T_h = 298 K; V_{bomb} = 0.2664 L; p^i_{gas} = 30.45 bar; m^i_{water} = 0.78 g; $E_{ignition}$ = 1.5 J; m_{platin} = 9.77 g. Microcalorimeter: T_h = 298 K; V_{bomb} = 0.0460 L; p^i_{gas} = 30.45 bar; m^i_{water} = 0.23 g; $E_{ignition}$ = 1.5 J; m_{platin} = 2.37 g. [b] Corrected masses obtained from weight by calculating the buoyancy. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$, ϵ_{calor} = 25 088.9 ± 2.6 J K^{-1} (0.010%) for **1**−**3** (in macro), ϵ_{calor} = 1403.86 ± 0.22 J K^{-1} (0.015%) for **3** (in micro), from calibration with benzoic acid; $\epsilon_{cont}(-\Delta T_c) = \epsilon^i_{cont}$ (T^i − 298 K) + ϵ^f_{cont} (298 K − T^f + ΔT_{corr}). [d] ΔE_{corr} is sum of items 81−85, 87−90, 93, and 94 in ref 11.

Table 4. Specific Energies of Combustion $-\Delta u_c^\circ$ (J g^{-1}) as the Result of All Combustion Experiments for Compounds 1−3

1	2	3[a]	3[b]
47 645.3	47 747.4	47 794.7	47 812.7
47 598.0	47 779.2	47 791.3	47 874.2
47 618.9	47 790.5	47 629.8	47 847.4
47 656.6	47 731.1	47 716.0	47 752.5
47 624.8	47 758.3	47 737.3	47 802.2
	47 719.4		
	47 729.8		
mean value:			
47 628.7	47 750.8		47 775.8

[a] Experiments in the macrocalorimeter. [b] Experiments in the microcalorimeter.

CDCl$_3$) δ 11.0 (CH$_3$), 27.5 (CH$_2$), 44.0 (C); MS (70 eV) m/z 99 (10, M$^+$/2), 57 (100, C$_4$H$_9$$^+$). Anal. Calcd for C$_{14}H_{30}$ (198.39): C, 84.76; H, 15.24. Found: C, 84.57; H, 15.05. The product was purified by distillation in a spinning band column, bp 80 °C (0.6 Torr). After purification, no impurities >0.001% could be detected in the sample by GC.

2,2,3,3,4,4,5,5-Octamethylhexane (2). A 3.97 g (16%) sample of **2** was obtained by irradiation of 25 g of 2,2,3-trimethylbutane under reflux for 18 d (generation of 1.8 L of hydrogen) and distillation of the residue: ^{1}H-NMR (250 MHz, CDCl$_3$, TMS) δ 1.00 (s, 18 H, C(C*H*$_3$)$_3$), 1.18 (s, 12H, C(C*H*$_3$)$_2$C); ^{13}C NMR (20 MHz, CDCl$_3$) δ 22.73 (*C*H$_3$)$_2$C, 30.01 (*C*H$_3$)$_3$C, 41.43 ((CH$_3$)$_2$*C*, 46.47 (CH$_3$)$_3$*C*; MS (70 eV) m/z 141 (9, M$^+$ − C$_4$H$_9$$^+$), 99 (19, M$^+$/2), 57 (100, C$_4H_9$$^+$). Anal. Calcd for C$_{14}H_{30}$ (198.39): C, 84.76; H, 15.24. Found: C, 84.45; H, 15.42. The product was purified in a spinning band column, bp 65 °C (0.6 Torr) [lit.[9d] bp 102 °C (12 Torr)], purity >99.94%.

Tri-*tert*-Butylmethane (3) was prepared and purified by recrystallization and sublimation by the previous procedure,[12] mp 83 °C. After purification, no impurities (>0.001%) could be detected in the sample of **1** by GC.

Combustion Calorimetry. Compounds **1** and **2** were stable under bomb conditions. Tri-*tert*-butylmethane (**3**) is sensitive to oxygen; therefore, the preparation of the samples for combustion experiments was performed in a glovebox under N$_2$. The combustion experiments for the liquids **1** and **2** and the solid sample of **3** were performed in sealed mylar bags in a macrocalorimeter[1] with a stirred water bath. Measurements of the heat of combustion of **3** were, in addition, performed in an isoperibolic microcalorimeter,[10] and no differences between both series of measurements were found. The energy equivalents of the calorimeters were calibrated with a standard reference sample of benzoic acid (sample SRM 39i, National Bureau of Standards). Conventional procedures[11] were used for the reduction of the data to standard conditions. The densities of the substances were determined with the suspension method. The specific heat capacities were measured by DSC (Table 2).

Table 5. Vapor Pressures p Determined by the Transpiration Method

	T^a (K)	m^b (mg)	$V_{N2}{}^c$ (L)	p^d (mbar)	$\Delta H^\circ_{vap,T}$ or $\Delta H^\circ_{sub,T}$ [e] (kJ mol^{-1})
1	282.9	9.07 × 10^{-2}	2.126	5.434 × 10^{-3}	63.9 ± 1.2
	287.2	1.17 × 10^{-1}	1.733	8.540 × 10^{-3}	
	293.0	1.48 × 10^{-1}	1.264	1.473 × 10^{-2}	
	297.3	1.15 × 10^{-1}	0.696	2.075 × 10^{-2}	
	302.3	1.72 × 10^{-1}	0.642	3.358 × 10^{-2}	
	303.0	9.20 × 10^{-2}	0.340	3.391 × 10^{-2}	
	307.3	8.90 × 10^{-2}	0.240	4.644 × 10^{-2}	
2	288.9	2.92	17.890	2.303 × 10^{-2}	56.90 ± 0.70
	299.3	1.29	3.200	5.298 × 10^{-2}	
	299.3	2.12	5.280	5.310 × 10^{-2}	
	304.3	1.73	2.810	7.898 × 10^{-2}	
	304.3	1.29	2.280	7.361 × 10^{-2}	
	314.4	1.44	1.190	1.545 × 10^{-1}	
	319.4	1.72	0.945	2.308 × 10^{-1}	
	324.5	1.49	0.610	3.072 × 10^{-1}	
3	264.7	1.09	14.060	1.050 × 10^{-2}	57.03 ± 0.43 (sublimation)
	272.9	5.39 × 10^{-1}	3.171	2.297 × 10^{-2}	
	278.5	2.44	8.210	4.110 × 10^{-2}	
	279.1	5.34 × 10^{-1}	1.760	4.085 × 10^{-2}	
	283.6	2.11	4.760	6.079 × 10^{-2}	
	284.6	3.22 × 10^{-1}	0.599	7.236 × 10^{-2}	
	288.6	2.08	3.070	9.195 × 10^{-2}	
	293.5	2.21	2.140	1.400 × 10^{-1}	
	298.4	3.20	2.090	2.069 × 10^{-1}	
	303.3	2.48	1.130	2.964 × 10^{-1}	
	308.4	3.61	1.180	4.120 × 10^{-1}	
	313.7	3.86	0.837	6.209 × 10^{-1}	
	318.6	4.00	0.619	8.687 × 10^{-1}	

[a] Temperature of saturation, N$_2$ gas stream 0.95−1.88 L h^{-1}. [b] Mass of transferred sample by cooling to the temperature of condensation T_{cond} = 243 K. [c] Amount of nitrogen used to transfer the mass m of the sample. [d] Vapour pressures at temperatures T of experiment, corrections for residual vapor pressure at T_{cond} were made. [e] T corresponds to to the average of the temperature applied for the measurements (see column 2).

Results for typical combustion experiments of each compound are given in Table 3. The individual values of the specific enthalpies of combustion and the mean values are listed in Table 4.

Enthalpies of Vaporization or Sublimation. Transpiration Method. The enthalpies of vaporization ΔH_{vap}° of **1** and **2** and of sublimation ΔH_{sub}° for **3** were determined by means of the method of transference in a saturated N$_2$ stream.[13,14] The substances were mixed with glass beads and filled into a thermostated U-shaped tube. At several temperatures, a slow stream of nitrogen was passed through the U-shaped tube, and the transported amount of material was condensed in a trap cooled to −30 °C. Its mass was determined by GC analysis after addition of an internal standard, and the

vapor pressure p was calculated from these data and the residual vapor pressure at the condensation temperature.[13] The latter and the enthalpies of sublimation or vaporization, respectively, were calculated by the following equation: $\Delta H_{vap}° = -R[\mathrm{d} \ln (p)/\mathrm{d}T]$ (with R = gas constant, T = temperature). The enthalpies of vaporization and sublimation at 298 K are recorded in Table 5.