Strain Energies in [n]Triangulanes and Spirocyclopropanated Cyclobutanes: An Experimental Study

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Abstract: The enthalpies of formation for trispiro[2.0.0.2.1.1]nonane (3), [3]rotane (4), *n*-heptyl[3]rotane (6), spiro-[2.3]hexane (7), and the isomeric dispiro[2.0.2.2]octane (8) and dispiro[2.1.2.1]octane (9), as well as [4]rotane (10), have been determined by measuring their heats of combustion in a microcalorimeter; these values and the strain energies (SE) derived from them are compared with values for MM2/MM3 calculations. The results confirm previously reported theoretical and experimental values for spiropentane and establish an additivity scheme for strain energies in all sorts of [n]triangulanes, with an excessive strain energy increment of 8.6 kcal/mol per spiro carbon atom. Such an additional strain increment is virtually nonexistent for 7 (0.8 ± 0.4 kcal/mol), 8 (0.6 ± 0.2 kcal/mol), and 9 (0.3 ± 0.3 kcal/mol) but is significant for 10, with $\Delta SE = 2.4 \pm 0.5$ kcal/mol. Therefore, a simple additivity of strain energies without an excess increment can be employed for spirocyclopropanated cyclobutanes as well as larger rings including [n]rotanes (n > 4).

The concept of strain¹ and strain energies provides a basis that helps to correlate the structures, stabilities, and reactivities of molecules.^{2.3} A quantitative assessment of strain and strain energies (SE) can be made only by taking the difference between the enthalpy of formation, $\Delta H_f^{\circ}(g)$, of the substance under consideration (theoretically calculated or experimentally determined) and that of a hypothetical strain-free model.² Basically, there are two approaches, based on an additivity of (i) bond energies (BE) and (ii) group increments (GI) (for details, see refs 2 and 3).

In the period of almost 100 years since the first preparation of spiropentane (1),⁴ spiro-condensed three-membered ring systems such as 1-4, consisting exclusively of spiro-attached three-membered rings ([n]triangulanes, with n indicating the number of cyclopropane rings⁵), have been the subject of numerous investigations.⁶ The series of homologous hydrocarbons 7-10, all spirocyclopropanated cyclobutanes, has also received a good deal of attention. Both 4 and 10 are also members of the interesting family of hydrocarbons named [n]rotanes:⁷ 4 is [3]rotane⁸ and 10 is [4]rotane. It has only been during the past 25 years that synthetic approaches to polyspi-

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ranes 2-4,⁹ 5,⁵ 7,¹⁰⁻¹² 8, 9,¹³⁻¹⁵ and $10^{13,16-19}$ have been elaborated. A number of theoretical and experimental studies were focused primarily on the quantitative estimation of

(8) [3]Rotane (4) is the only compound which counts as a member of both families -[n] triangulanes and [n] rotanes.

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structural parameters (1-4, ref 9; 7, refs 20-22; 8 and 9, ref 20; and 10, refs 20, 23-25) as well as the bonding properties (1, 2, 4, ref 9; 7-9, refs 11 and 20; and 10, refs 20, 26, and 27) in such hydrocarbons. The theory of the energetics of such compounds has been probed predominantly for spiropentane (1),⁹ the only triangulane for which an experimental value was available until recently (see Table 1). Two different measurements of the $\Delta H_f^{\circ}(g)$ for 1 have been reported;²⁸ however, the second value of 44.23 kcal/mol^{28b} is now generally accepted.

Dewar et al. stressed for the first time that the strain energy of **1** should be more than double that of cyclopropane;^{29a} i.e., the spiro junction of two cyclopropane rings should lead to additional strain. In fact, the experimental values of SE for 1 (65.1 kcal/mol^{28b}) and cyclopropane (28.1 kcal/mol³⁰) based on the same strain-free model³⁰ lead to an excessive incremental strain energy of $\Delta SE = 8.9$ kcal/mol [65.1 - 2(28.1)]. Apparently, the same excess increment should be applicable ntimes for a triangulane with n spiro carbon atoms with $\Delta SE =$ 8-10 kcal/mol, as predicted by MM2 calculations.²³ In this context, the interesting question arises of whether the excessive incremental strain energy ΔSE really stays constant, independent of the number of spiro atoms in a given system and independent of the relative position of the spiro carbon in the molecule. The values of ΔSE , calculated on the basis of recently reported experimentally determined $\Delta H_f^{\circ}(g)$ for 2-4,³¹ are equal to 7.1 kcal/mol for 2 {[98.52 - 3(28.13)]/2}, 7.3 kcal/mol for 3 and 6.6 kcal/mol for 4 and 5. This seems to indicate that ΔSE would, indeed, depend on the number of spiro atoms as well as their position in a molecule, and it would mean that a general additivity scheme for strain energies cannot be applied to [n]triangulanes. As we could not conceive of any reasonable explanation for this phenomenon, we set out to redetermine the heats of combustion for 3 and 4 and include the derivative 6 in the study.

Regarding the spirocyclopropanated cyclobutane derivatives 7-10, their energetic characteristics are very little documented; the authors of numerous theoretical investigations refer to the lack of experimental data for comparison. The absolute energy values calculated for compounds 7-10 by CFF PEF304 and

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PEF404 methods³² tell us very little about the relative stability of these hydrocarbons. MM2 and MM3 calculations yield two different results for 10 that cannot be compared (Table 1). Therefore, we have also determined the heats of combustion for compounds 6-10 for the first time.

The hydrocarbons 3, 4,⁹ 7,¹⁰ and 10^{13,18} were prepared by known methods; compound 6 was obtained from *n*-heptylbicyclopropylidene (11)⁴⁷ in three steps according to one of the published procedures for [3]rotane⁹ (Scheme 1), namely addition of chloromethylcarbene⁴⁸ to 11, dehydrochlorination of the resulting 12 with *t*-BuOK/DMSO,⁴⁸ and subsequent cyclopropanation of 13 with diazomethane in the presence of palladium(II) acetate.⁴⁹ New synthetic approaches have been elaborated for compounds 8 and 9 (Scheme 1).

The results of all thermochemical measurements are summarized in Table 1 (for details, see Experimental Section). The new data show that the difference SE – $[4SE(C_3H_6)]$ is equal to 25.7 kcal/mol for **3** and 25.1 kcal/mol for **4**, corresponding to excess increments, Δ SE, of 8.6 and 8.4 kcal/mol per spiro junction, respectively. The experimental value for *n*-heptyl[3]rotane (**6**), which is less reliable because of incomplete combustion,⁵⁰ yields Δ SE = 7.2 kcal/mol. The mean value for **3** and **4** is 8.5 kcal/mol per spiro atom, within the limits of error essentially the same as that for **1**. These results indicate that all types of spiro atoms in [*n*]triangulanes contribute the same additional strain and that a general additivity scheme can be applied to calculate total strain energies for such compounds. Assuming that this additivity scheme also holds for higher [*n*]triangulanes, one can assess their SEs according to eq 1.

SE = n28.1 + (n - 1)8.6 [kcal/mol] (1)

In this equation, the mean value for the whole series 1, 3, 4 should be applied; *n* denotes the number of cyclopropane units (every [n]triangulane has (n - 1) spiro atoms). For example,

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Table 1.	Comparison of	Thermochemical	Data for 1.	-10 According	; to Theoretic	al and Experimentation	al Investigations (All	Values in kcal/mol)

compound	method	$\Delta H_{\rm f}^{\rm o}({\rm g})$	SE	ref
<u> </u> C ₃ H ₆	expt	12.74	28.13 ^e	30, 33
C ₄ H ₈	expt	6.38	26.90 ^e	30, 33
\bowtie	MM2	43.96	63.61	34
	MM2	43.97		35
1	MM2	43.96	63.3, ^{<i>a</i>} 64.0, ^{<i>b</i>} 63.31 ^{<i>d</i>}	23
	MM2	44.34		36
	MM3	43.83		37
	MM3	44.15		36
	MM/2ER W	44.45	AE 6a	20 28
	MINDO/3	28.7	45.0"	29, 38
	SCE MO	58.0	75.2	29b
	STO-3G	43.8	63 7 ^b	40
	3-216	48.60	03.7	41
	4-31G	45.50	65.4^{b}	40
	4-31G	44.08		41
	6-31G*	42.62	61.4 ^c	42
	expt	41.77 ± 0.31	62.59 ± 0.31	28a, 30
	expt	44.23 ± 0.18	65.05 ± 0.18^{e}	28b, 30
^	MM2	76.0	99 8 ^a 100 42 ^d	23
	MMX 88	76.0	, xoona	5
\vee \vee	MINDO/3		69.9 ^a	38
2	expt	72.27 ± 0.83	98.52 ± 0.83^{e}	31
A A	MM2	107.07	126 2 a 127 5d	22
	MM2	107.97	142 06	25 this work
\vee \vee	MM3	102.3	133.1	this work
3	expt	102.6 ± 1.6	134.28 ± 1.6^{e}	31
-	expt	106.57 ± 0.19	138.25 ± 0.19^{e}	this work
	NANA 2	100.10	127 1 a 120 2 b 128 28d	23
X	MM2	109.79	140.0	this work
$ \longrightarrow $	MM3	101.2	132.0°	this work
\vee \vee	MINDO3	10112	95.21 ^a	38
4	expt	101.1 ± 1.17	132.18 ± 1.17^{e}	31
·	expt	105.91 ± 0.32	137.59 ± 0.32^{e}	this work
A A	MMX 88	139.85		5
$\rightarrow \rightarrow $	expt	129.83 ± 1.62^{f}	166.94 ± 1.62^{e}	31
\vee \vee \vee	I.			
5				
-		(0.71	120 444	
^C_7H_15	MM2 MM3	68.71 62.24	138.44*	this work
\mathbf{V}	expt	64.99 ± 0.69	132.08° 134.7 + 0.69°	this work
$-\Delta$	expt	04.97 - 0.07	134.7 ± 0.09	uns work
\vee \vee				
6				
<u>ه ۸</u>	MM2	29.71		35
\bowtie	expt	29.93 ± 0.38	55.85 ± 0.38^{e}	this work
•				
7				
	expt	53.0 ± 0.15	84.33 ± 0.15^{e}	this work
8		50.41.4.0.01		
\searrow	expt	52.41 ± 0.31	$83.75 \pm 0.31^{\circ}$	this work
9				
∇	MM2	85.29	125.0, ^{<i>a</i>} 125.4, ^{<i>b</i>} 122.9 ^{<i>a</i>}	23
\sim	MM2	85.30	127.54 ^e	this work
$\vee \vee \vee$	MM3	178.7	220.94 ^e	this work
Δ	MINDO/2		143	13
10	expt	106.61 ± 0.49	148.85 ± 0.49^{e}	this work

^{*a*} GI method according to Benson.^{43 *b*} "Homodesmotic" BE method according to George.^{44,45 *c*} GI method according to Wiberg.^{41,42 *d*} BE method according to Allinger.^{46 *e*} GI method according to Schleyer.^{30 *f*} A mixture of *meso*-**5** and (*d*,*l*)-**5** was used in the combustion.

the recently reported [10]triangulane 22, which is thermally stable up to 250 °C,51 according to eq 1 would possess a total SE of 358.4 kcal/mol. Using the homodesmotic reaction in Scheme 2, the predicted $\Delta H_{f}^{\circ}(g)$ is 274.2 kcal/mol, and the isodesmic ring separation reaction with methane that leads to separated rings⁵² in its modification for spiro compounds⁴⁰ affords $\Delta H_{RS}^{\circ} = 288.4$ kcal/mol (for a definition of the terms "isodesmic" and "homodesmotic", see ref 2, p 7). In view of

Scheme 1



Scheme 2. Homodesmotic Reaction for [10]Triangulane 22 To Estimate Its $\Delta H_f^{\circ}(g)$



these values, the thermodynamic driving forces for thermal reorganizations of triangulanes ought to be strong. Surprisingly, however, many of the known triangulanes enjoy a remarkable thermal stability. For example, the thermal rearrangement of spiropentane (1) is observed only at temperatures above 350 °C and requires an activation energy of 57.6 kcal/mol.⁵³ For comparison, cubane with its strain energy between 157^{54a} and 161 kcal/mol.^{54b} and $\Delta H_f^{\circ}(g)$ between 148.7^{54a} and 158.8 kcal/mol.^{54b} is thermally stable up to 220 °C.⁵⁵ The [*n*]triangulanes, therefore, present another convincing example for the well-known fact that total strain energy of a molecule and kinetic instability do not correlate at all.

With respect to the thermochemical properties of spirocyclopropanated cyclobutanes, it is remarkable that MM2 calculations yield a $\Delta H_{\rm f}^{\circ}(g)$ value for spiro[2.3]hexane (7) which is almost identical with the experimental one $(29.71^{35} vs 29.93)$ kcal/mol). But neither the MM2 nor the MM3 force field appears to be appropriate for [4]rotane (10), with calculated values of 85.3 (MM2) and 178.7 kcal/mol (MM3), compared to the experimental one of 106.6 kcal/mol (see Table 1). The value of 143 kcal/mol, calculated for the strain energy in 10 with the MINDO/2 method,¹³ is sufficiently close to the experimental one (148.9 kcal/mol). In contrast, both the MM2 and MM3 methods give good results for triangulanes 1-4 and 6. Moreover, whereas the enthalpies of formation for 1-4 can be evaluated quite satisfactorily using the isodesmic ring separation reaction 3 (Scheme 3), the analogous reaction 4 cannot be applied for the series of spirocyclopropanated Scheme 3. Comparison of Experimentally Determined $\Delta H_f^{\circ}(\mathbf{g})$ for [n]Triangulanes (n = 1-3) with Calculated $\Delta H_{\text{RS}}^{\circ}$ Using the Ring Separation Reaction 3 (All Values in kcal/mol)^a

$$(\bigcup_{n=1}^{n} + n CH_4 \longrightarrow (n+1) < (3)$$
23

Compound	1 (<i>n</i> =1)	2 (<i>n</i> =2)	3 (<i>n</i> =3)	4
∆H ^e _{RS}	43.37	74.0	104.63	104.63
$\Delta H^{o}_{f}(g)_{exp.}$	44.23	72.27	106.57	105.91

 a Calculated with $\Delta H_{f}^{\circ}(g)$ = 12.74 for C_{3}H_{6}; -17.89 kcal/mol for CH_{4}.^{30,43}

Scheme 4. General Isodesmic (4) and Homodesmotic (5) Reactions for Spirocyclopropanated Cyclobutanes To Estimate Their ΔH_{RS}° and $\Delta H_{f}^{\circ}(g)$ (All Values in kcal/mol)^{*a*}



 a Calculated with $\Delta H_f^\circ(g)=6.38$ for $C_4H_8;$ -17.89 for CH4; 12.74 kcal/mol for $C_3H_6.^{30.43}$

cyclobutanes 7–10 (Scheme 4). The homodesmotic reaction 5 in Scheme 4, describing the energetic interrelations for the whole series of spirocyclopropanated cyclobutanes 7–10, also demonstrates a substantial underestimation of $\Delta H_{\rm f}^{\circ}(g)$ for [4]rotane (10).

The other important question is the excess incremental strain contribution (Δ SE) of a spiro junction between a three- and a four-membered ring. In compounds 7-9, this contribution is practically negligible in comparison with that for triangulanes $(\Delta SE(7) = 0.8 \pm 0.4, \Delta SE(8) = 0.6 \pm 0.2, \text{ and } \Delta SE(9) = 0.3$ \pm 0.3 kcal/mol), but for 10, this destabilizing effect is significant, with $\Delta SE = 2.4 \pm 0.5$ kcal/mol {[148.85 - (4(28.13)] + 26.90)]/4}, yet much smaller than that in [n]triangulanes. The difference between compounds 7-9 on one side and 10 on the other must have to do with the fact that cyclobutane⁵⁶ and spiro-[2.3]hexane $(7)^{57}$ are not planar, while an increasing number of spiro-fused cyclopropane rings must result in an increasing force for planarization⁵⁷ at the expense of increasing additional strain. But even the overall effect for four spirocyclopropanes is rather small, and with respect to the error limits, the subtle differences between 7, 8, and 9 cannot be accounted for. Essentially, then, a simple additivity of ring strain energies without an excess increment can be applied for spirocyclopropanated cyclobutanes 7-9 and probably also spirocyclopropanated larger rings, including higher [n] rotanes (n > 4), whereas in [4] rotane (10), a significant contribution from the four spiro junctions is noticed.

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⁽⁵⁷⁾ The puckering angle α in spiro[2.3]hexane (7) in the crystal²¹ is 21°, i.e., slightly smaller than that in cyclobutane, with $\alpha = 27.5^{\circ}.5^{\circ}$ Dispiro-

^[2.1.2.1] octane (9) is planar in the crystalline state (cf.: Boese, R.; Haumann,

T., unpublished results), as is tetraspiro[2.0.2.0.2.0.2.0]dodecane (10).25c

Experimental Section

General. Compounds 4 and 10 were purified by column chromatography (silica gel, pentane), followed by recrystallization from methanol and repeated (2-3 times) sublimations under reduced pressure, and compounds 3, 6-9 by repeated (2-3 times) preparative gas chromatography (20% SE 30 on Chromaton W-AW-DMCS, 3500 mm \times 8.2 mm column), followed by distillation over 4 Å molecular sieves. The purity (\geq 99.95%) was checked by GC and DSC analyses. ¹H and ¹³C NMR spectra (with additional DEPT) were recorded in CDCl₃ at 250 and 62.9 MHz, respectively; coupling constants (J) are given in hertz. ¹H NMR spectra for compounds 3, 4,⁹ 7,¹² 8, 9,¹³ and 10^{13,17,19b} and their synthetic precursors 14^{19a} and 15¹³ have been reported. ¹³C NMR for 7, δ 17.07 (CH₂), 12.09, 30.82 (2 CH₂), 19.93 (C); 8, δ 8.87, 27.68 (CH₂), 24.59 (C); 9, δ 12.40, 39.71 (CH₂), 15.38 (C); 10, δ 6.02 (CH₂), 28.73 (C); 14, δ 3.17 (CH₂), 60.48 (C); 15, δ 16.28 (2 CH₂), 20.48, 43.75 (CH₂), 39.51, 215.06 (C); and 17, δ 17.75, 40.58 (CH₂), 25.0 (C). The relative configurations of compounds 12 and 13 have not actually been determined.

endo-7-Chloro-7-methyl-1-n-heptyldispiro[2.0.2.1]heptane (12). To a stirred solution of 15.50 g (86.9 mmol) of olefin 11 and 17.20 g (11.9 mL, 174 mmol) of 1,1-dichloroethane in Et₂O (40 mL) at -30°C was added 61 mL (174 mmol, 2.85 M in hexane) of BuLi over a period of 2 h. The mixture was poured into 100 mL of ice-cold H₂O, and the aqueous layer was extracted with Et₂O (100 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by vacuum distillation to give 12.58 g (60%) of 12 as a 1:1 mixture of two stereoisomers: bp 97-103 °C (1 mmHg); ¹H NMR δ 0.39 and 0.51 (t, J = 4.8, 1 H), 0.61 - 0.68 and 0.74 - 0.81 (m, 1 H), 0.81 - 0.94(m, 4 H), 0.94–1.05 (m, 3 H), 1.05–1.20 (m, 3 H), 1.20–1.45 (m, 10 H), 1.52 and 1.56 (s, 3 H); 13 C NMR δ 5.60, 5.95, 6.01, 6.53, 12.30, 12.91, 22.73, 29.37, 29.47, 29.56, 29.60, 29.82, 31.68, 31.72, 31.96 (CH₂), 14.13, 23.77, 23.96 (CH₃), 20.47, 20.86 (CH), 24.88, 29.95, 49.97, 50.10 (C); MS (CI/NH₃) calcd for C₁₅H₂₉ClN (MNH₄⁺) 258, 260; found 258, 260.

endo-7-Methylene-1-*n*-heptyldispiro[2.0.2.1]heptane (13). A solution of chlorides 12 (10.35 g, 43.0 mmol) and *t*-BuOK (5.79 g, 51.6 mmol) in DMSO (150 mL) was stirred for 48 h at room temperature with GC monitoring and then poured into 200 mL of ice-cold H₂O. The aqueous layer was extracted with pentane (3 × 50 mL); the combined organic extracts were washed with H₂O (3 × 50 mL), dried over MgSO₄, and concentrated under reduced pressure. Vacuum distillation gave 7.03 g (80%) of 13: bp 83–85 °C (1 mmHg); ¹H NMR δ 0.67–0.72 (m, 1 H), 0.85–1.0 (m, 5 H), 1.0–1.13 (m, 2 H), 1.13–1.25 (m, 4 H), 1.25–1.55 (m, 10 H), 4.98–5.01 (m, 2 H); ¹³C NMR δ 7.95, 8.79, 15.72, 22.75, 29.47, 29.55, 29.60, 31.76, 31.98, 93.18 (CH₂), 14.16 (CH₃), 23.43 (CH), 14.59, 19.66, 142.63 (C); MS (CI/NH₃) calcd for C₁₅H₂₈N (MNH₄⁺) 222; found 222.

1-n-Heptyltrispiro[2.0.2.0]nonane (6). To a stirred solution of olefin 13 (6.81 g, 33.3 mmol) and Pd(OAc)₂ (370 mg, 1.65 mmol) in Et₂O (50 mL) at 0 °C was added diazomethane (prepared from 34.3 g (0.333 mol) of N-nitrosomethylurea and a solution of 80.89 g (1.44 mol) KOH in H₂O (300 mL) at -5 °C as a solution in 300 mL of Et₂O) over a period of 2 h. After being left to stand overnight, the solution was filtered through silica gel (25 g) and concentrated under reduced pressure to afford 7.26 g (100%) of crude 6. Vacuum distillation gave 7.12 g (98%) of 6 in 97.7% purity (GC): bp 92.5 °C (1 mmHg); ¹H NMR δ 0.38 (t, J = 4.4, 1 H), 0.64–0.85 (m, 8 H), 0.78-0.83 (dd, J = 4.1, 7.7, 1 H), 0.83-0.95 (m, 1 H), 0.89 (t, J = 0.78-0.83 (dd, J = 4.1, 7.7, 1 H), 0.83-0.95 (m, 1 H), 0.89 (t, J = 0.13 H) 5.3, 3 H), 1.02-1.18 (m, 2 H), 1.23-1.32 (m, 6 H), 1.32-1.45 (m, 4 H); ¹³C NMR δ 4.06, 4.47, 4.67, 4.79, 10.97, 22.76, 29.46, 29.60, 29.72, 31.92, 32.0 (CH₂), 18.93 (CH), 14.20 (CH₃), 17.52, 18.73, 22.51 (C). Anal. Calcd for C₁₆H₂₆: C, 88.00; H, 12.00. Found: C, 87.91; H, 12.08

4-Methylenespirohexane (16) was obtained according to the modified Wittig procedure.⁵⁸ To the stirred solution of triphenylphosphonium methylide, prepared from methyltriphenylphosphonium bromide (57.12 g, 0.16 mol) and NaH (3.84 g, 0.16 mol) in DMSO (75 mL), was added ketone **15** (11.20 g, 0.117 mol) at ambient temperature over

a period of 10 min. After being stirred over 0.5 h, the product was distilled *in vacuo* to the cold trap, washed with H₂O (2 × 10 mL), and dried over 4 Å molecular sieves to give 10.12 g (92%) of **16**, which contained about 5% of C₆H₆ (GC-NMR data): ¹H NMR δ 0.80 (m, 4 H), 2.20 (t, J = 6.8, 2 H), 2.78 (tt, J = 6.8, 2.1, 2 H), 4.39 (t, J = 2.1, 1 H), 4.55 (t, J = 2.1, 1 H); ¹³C NMR δ 15.71 (2 CH₂), 27.05, 28.28, 97.66 (CH₂), 27.27, 158.15 (C).

Dispiro[2.0.2.2]octane (8) was obtained using the modified Simmons–Smith procedure⁵⁹ (the method successfully applied for the preparation of 6 gave in this case a 1:1 mixture of olefin and product). To the stirred suspension of a Simmons–Smith reagent, prepared from Zn (30.90 g, 0.473 mol), CuCl (3.10 g, 31.3 mmol) and CH₂I₂ (53.53 g, 16.1 mL, 0.20 mol) in Et₂O (230 mL), was added 9.28 g (98.6 mmol) of olefin 16 over a period of 0.5 h under reflux. The reaction was monitored with GC. After 15 h under reflux, the volatile components of the reaction mixture were distilled "bulb-to-bulb" *in vacuo* to a cold trap, carefully concentrated using a 30 cm rectification column, and distilled under reduced pressure to afford 10.12 g (95%) of 8: bp 105 °C (500 mmHg).

Diethyl spirohexane-5,5-dicarboxylate (18) was prepared in 32% yield by alkylation of diethyl malonate with 1,1-bis(bromomethyl)cyclopropane (17) [obtained by bromination of the corresponding diol (easily prepared by reduction of a commercially available diethyl cyclopropane-1,1-dicarboxylate⁶⁰ with LiAlH₄ in 99% yield) with triphenylphosphane dibromide in 90% yield] according to the known procedure.⁶⁰ 17 (110.78 g, 0.486 mol), diethyl malonate (77.86 g, 73.8 mL, 0.486 mol), and powdered K₂CO₃ (268.3 g, 1.941 mol) were vigorously stirred in DMSO (800 mL) (70 °C, 15 h). After cooling, the mixture was poured into 2.5 L of ice-cold H₂O and extracted with Et_2O (3 \times 200 mL). The combined etherial solutions were washed with water (3 \times 300 mL), dried over MgSO₄, and concentrated under reduced pressure. Vacuum distillation afforded 35.29 g (32%) of 18: bp 113–115 °C (1 mmHg); ¹H NMR δ 0.37 (s, 4 H), 1.15 (t, J = 6.8, 6 H), 2.54 (s, 4 H), 4.12 (q, J = 6.8, 4 H); ¹³C NMR δ 13.78 (CH₃), 11.46, 37.12, 61.07 (CH₂), 14.47, 49.04, 171.38 (C). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.81; H, 8.05.

5,5-Bis(hydroxymethy)spirohexane (19). To a stirred solution of LiAlH₄ (4.67 g, 0.123 mol) in Et₂O (300 mL) was added diester **18** (27.94 g, 0.123 mol) at a moderate rate. The mixture was refluxed for 1 h, quenched with saturated aqueous Na₂SO₄ solution, and filtered. The precipitate was additionally extracted with Et₂O overnight using a Soxhlet extractor. The combined ethereal solutions were dried over 4 Å molecular sieves and concentrated under reduced pressure to give **19** (17.38 g, 99%) as an oil, which was used without purification. **19**: ¹H NMR δ 0.35 (s, 4 H), 1.80 (s, 4 H), 3.50 (s, 2 H), 3.73 (s, 4 H); ¹³C NMR δ 11.85, 35.43, 69.46 (CH₂), 14.49, 39.77 (C).

5,5-Bis{[(benzenesulfonyl)oxy]methyl}spirohexane (20). To a stirred solution of diol **19** (17.38 g, 0.122 mol) in pyridine (140 mL) was added benzenesulfonyl chloride (53.01 g, 38.3 mL, 0.3 mol) at -5 °C over 2 h. The mixture was stirred for an additional 12 h at this temperature and then poured into ice-cold 3 N HCl (500 mL). The precipitate was filtered and recrystallized from MeOH to give 33.61 g (65%) of **20**: mp 74–75 °C (from MeOH); ¹H NMR δ 0.30 (s, 4 H), 1.82 (s, 4 H), 4.08 (s, 4 H), 7.50–7.60 (m, 4 H), 7.60–7.70 (m, 2 H), 7.80–7.90 (m, 4 H); ¹³C NMR δ 11.33, 34.76, 71.98 (CH₂), 127.75, 129.25, 133.85 (CH), 14.10, 37.76, 135.48 (C). Anal. Calcd for C₂₀H₂₂O₆S₂: C, 56.85; H, 5.25. Found: C, 56.80; H, 5.32.

5,5-Bis(iodomethyl)spirohexane (21) was prepared adopting the published procedure.⁶¹ A solution of **20** (27.98 g, 66.2 mmol) and NaI (26.80 g, 179 mmol) in Et₂CO (200 mL) was refluxed overnight, poured into ice-cold H₂O (500 mL), and extracted with pentane (3 × 100 mL). The combined extracts were washed with water, 5% Na₂S₂O₃, and brine and dried over MgSO₄. The concentration under reduced pressure afforded 23.21 g (97%) of **21**: ¹H NMR δ 0.47 (s, 4 H), 2.03 (s, 4 H), 3.60 (s, 4 H); ¹³C NMR δ 11.38, 21.88, 39.93 (CH₂), 10.96, 39.70 (C). This substance was used without purification.

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Table 2.	Specific Energies of	Combustion (Δu_c)	Resulting from All	Combustion Ex	periments (cal/g)
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	3	4	6	7	8	9	10
	11 234.6	11 203.3	11 173.1	11 283.1	11 134.0	11 133.1	11 004.0
	11 230.4	11 194.5	11 151.4	11 264.4	11 131.4	11 145.6	10 993.0
	11 236.5	11 195.8	11 161.9	11 268.8	11 132.6	11 139.6	11 003.7
	11 234.9	11 202.5	11 162.5	11 250.5	11 136.3	11 135.0	10 986.9
	11 230.9	11 208.0	11 158.3	11 265.5	11 131.4	11 142.4	10 998.2
	11 118.4	11 208.5	11 162.8	11 269.0			10 987.1
							10 982.7
							10 987.7
							10 978.2
mean	11 232.6	11 202.1	11 161.6	11 266.9	11 133.1	11 141.3	10 991.3
SD^a	±1.3	± 2.4	± 2.9	± 4.3	± 0.9	±1.9	± 3.0
			-				

^a Standard deviation of the mean.

Table 3. Densities and Heat Capacities of Compounds 3, 4, and 6-10 at 25 °C

	3	4	6	7	8	9	10
$d (g/cm^3)^a c_p (cal/g·K)^b$	0.87	1.02	0.92	0.77	0.84	0.81	1.08
	0.51	0.32	0.42	0.47	0.39	0.40	0.25

^{*a*} Densities of the solid compounds (3 and 10) are determined by floating some crystals in a salt solution in ethanol/water of known density and the liquids by using a pyknometer. ^{*b*} Measured by DSC.

Table 4. Results of Typical Combustion Experiments^a

	3	4	6	7	8	9	10
calorimeter	macro	micro	micro	macro	macro	macro	micro
$m_{\rm sub}~({ m mg})$	146.114	29.911	29.260	339.787	328.371	345.443	35.941
$m_{\rm cotton} ({\rm mg})$	0.893	0.651	0.650	1.123	0.844	0.948	0.599
$m_{\rm oil} ({\rm mg})$	167.721						
$m_{\rm pe}$ (mg)	572.115			288.344	275.312	272.383	
m _{Mylar} (mg)		11.254	12.429				9.868
$\Delta T_{\rm c} ({\rm K})^b$	1.639 09	1.142 50	1.126 68	1.171 43	1.118 48	1.216 70	1.279 88
$\epsilon_{\rm calor} \Delta T_{\rm c} ({\rm cal})^c$	9828.29	398.970	396.897	7027.06	6709.44	7298.65	451.138
$\epsilon_{\rm cont} \Delta T_{\rm c} ({\rm cal})^d$	5.72	0.729	0.727	3.88	3.69	5.01	0.827
$\Delta E_{\rm corr} \Delta T_{\rm c} ({\rm cal})^e$	3.66	0.191	0.172	2.36	2.34	2.61	0.215
$m_{\rm fuse}\Delta u_{\rm c}({\rm cotton})~({\rm cal})^f$	-3.62	-2.64	-2.63	-4.55	-3.42	-3.65	-2.43
$m_{\rm oil}\Delta u_{\rm c}({\rm oil})$ (cal) ^f	1843.83						
$m_{\rm pe}\Delta u_{\rm c}({\rm pe})~({\rm cal})^f$	6340.98			3195.83	3051.39	3097.39	
$m_{\rm Mylar}\Delta u_{\rm c}({\rm Mylar}) ({\rm cal})^f$		-61.429	-67.842				-53.826
$\Delta u_{\rm c}({\rm sub})$ (cal)	11 234.9	11 202.5	11 161.9	11 265.5	11132.6	11 139.8	11 992.9

^a Notations see ref 64; weights in vacuum; $T_h = 25 \text{ °C}$, $T_f = 24.99 - 25.01 \text{ °C}$; $V_{bomb} = 0.046$ (micro) or 0.2664 L (macro); $p_{igas}^i = 30.00$ atm (30.40 bar) at 25.0 °C; $m_{H_2O}^i = 0.23$ (micro) or 0.78 g (macro); $E_{ign} = 0.36$ (micro) or 0.35 cal (macro); $m_{plainum} = 2.5$ (micro) or 4.7 (macro).^b $\Delta T_c = T_f - T_i + \Delta T_{corr.}$ c $\epsilon_{calor} = 25.088.10 \pm 1.05$ (3), 350.638 ± 0.069 (4), 352.255 ± 0.024 (6), 25.098.56 ± 1.77 (7–9), and 352.485 ± 0.058 (10). ^d $\epsilon_{cont} \Delta T_c = \epsilon_{cont}^i (T_i - T_h) + \epsilon_{cont}^i (T_h - T_f + \Delta T_{corr.})$. ^e Sums of items 81–85, 87–90, 93, and 94 in ref 64. ^f Δu_c (cotton) = -4050.0 ± 4.0 cal/g; Δu_c (oil) = -10.993.5 ± 1.7 cal/g; Δu_c (pe) = -11.083.38 ± 0.66 cal/g; Δu_c (Mylar) = -5458.6 ± 1.1 (1–4.64F) cal/g, F = relative humidity of the air (%).

Dispiro[2.1.2.1]octane (9) was prepared adopting the method of McGreer.¹⁰ To a stirred refluxing mixture of titriplex III (71.81 g, 0.193 mol), NaOH [a solution of 25.31 g (0.633 mol) in 40 mL of H₂O], EtOH (140 mL), and NaI (2.05 g, 13.7 mmol) were added Zn (18.81 g, 0.288 mol) in one portion and then diiodide 21 (23.03 g, 63.6 mmol) over a period of 1 h. After additional reflux over 1 h, the mixture was cooled, poured into ice-cold H₂O (500 mL), and extracted with pentane (3 × 100 mL). The combined extracts were washed with water, saturated aqueous NH₄Cl solution, and brine and then dried over MgSO₄. The pentane was carefully evaporated using a 30 cm rectification column, and the residue was distilled to give 9 (5.23 g, 76%): bp 103 °C.

Thermochemical Measurements. The heat of combustion measurements were performed either in an aneroid isoperibilic microcalorimeter⁶² or an isoperibilic macrocalorimeter of the stirred liquid type.⁶³ Calibration experiments were performed with benzoic acid (NBS, standard reference sample 39i). The crystalline compounds **4** and **10** were pressed into pellets, and all samples were sealed in bags. For the macrocalorimeter, the bags were made from pipets of polyethylene **Table 5.** Molar Enthalpies of the Crystalline (c) and Liquid (l)Compounds^a (kcal/mol)

	ALLP(a)h	A 11 0/11h	AURAN	A 77 0/1\/c	ATT d	Att d	A 11 -
	Δn _c ⁻ (c)"	$\Delta n_{\rm c}^{-}(1)^{\rm b}$	ΔΠf [*] (C) ^c	$\Delta n_{f}(1)$	Δn_{sub}	Δn_{vap}	ΔΠ _{fus} ^e
3		-1351.89		95.54		11.07	
		(± 0.18)		(± 0.18)		(±0.07)	
4	-1348.11		91.77			14.14	3.38 ^f
	(± 0.30)		(±0.30)			(± 0.12)	(±0.09)
6	-2441.21		48.29			16.78	
	(±0.65)		(± 0.65)			(± 0.10)	
7	-927.01		5.05			8.84	
	(±0.36)		(±0.36)			(±0.17)	
8	-1206.21		43.92			9.16	
	(±0.14)		(± 0.14)			(±0.17)	
9	-1207.10		44.80			7.69	
	(± 0.22)		(±0.22)			(± 0.22)	
10	-1763.85		88.72		17.89		5.02 ^g
	(±0.56)		(± 0.56)		(± 0.11)		(±0.06)

^{*a*} Standard deviation in brackets. ^{*b*} Standard enthalpies of combustion obtained from the specific heats of combustion in Table 2. ^{*c*} Standard enthalpies of formation obtained from $\Delta H_c^{\circ}(1 \text{ or } c)$. ^{*d*} Enthalpies of sublimation and enthalpies of vaporization obtained from the vapor pressure given in Tables 6 and 7. ^{*e*} Enthalpies of fusion measured by DSC. ^{*f*} Melting point, 38.9 °C. ^{*s*} Melting point, 121.7 °C.

(pe), and for the microcalorimeter, Mylar bags were used, which have been decribed earlier.⁶⁴ The addition of mineral oil as an auxiliary material had no influence on the results obtained, and no soot was

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Table 6. Vapor Pressure p of Compounds 3, 4, 6, and 10 as Measured by Flow Method^a

		30		4 ^c				
$\overline{T_{\text{sat}}(^{\circ}\text{C})}$	<i>V</i> (1)	m _{sub} (mg)	p (Torr)	T _{sat} (°C)	<i>V</i> (1)	m _{sub} (mg)	p (Torr)	
1.6	1.114	3.544	1.18	0.3	1.61	7.76	0.777	
6.5	0.907	9.43	1.70	2.2	1.58	8.86	0.900	
11.2	0.653	9.62	2.37	5.1	1.92	1.52	1.26	
16.0	0.541	11.3	3.32	10.0	0.126	1.99	1.93	
21.1	0.430	12.4	4.54	15.0	0.277	5.29	2.98	
26.2	0.338	13.0	6.03	20.0	0.228	6.57	4.49	
31.3	0.223	12.1	8.49	25.0	0.162	7.12	6.84	
36.3	0.111	8.26	11.6	30.1	0.113	7.53	10.3	
41.3	0.063	6.22	1.54	35.0	0.064	5.83	14.1	
		6 ^c				10 ^c		
$T_{\rm sat}$ (°C)	<i>V</i> (1)	m _{sub} (mg)	p (Torr)	$\overline{T_{\rm sat}(^{\circ}{\rm C})}$	<i>V</i> (1)	m _{sub} (mg)	p (Torr)	
25.1	45.7	4.11	0.00769	25.0	4.12	1.44	0.0428	
28.1	34.9	4.27	0.0104	30.0	3.61	2.12	0.0719	
35.0	15.4	3.57	0.0197	35.0	4.05	3.87	0.117	
40.0	6.69	2.41	0.0307	39.9	1.67	2.54	0.186	
45.0	4.10	2.25	0.0468	45.1	1.110	2.63	0.290	
50.0	3.69	3.09	0.0713	50.1	0.762	2.97	0.476	
55.0	1.99	2.38	0.102	55.0	0.514	2.94	0.700	
60.0	0.942	1.67	0.151	60.1	0.366	3.11	1.04	
				65.1	0.234	2.93	1.53	

^a Notation, see text; $T_{cond} = -30$ °C. ^b $\nu = 1.95$ L/h. ^c $\nu = 1.76$ L/h.

Table 7. Vapor Pressure p of Compounds **7–9** at Temperature T as Measured by DSC

	7		8	9		
$T(^{\circ}C)^{a}$	p (mbar)	$T(^{\circ}C)^{a}$	p (mbar)	$T(^{\circ}C)^{a}$	p (mbar)	
60.0	1010	95.7	500	88.9	500	
43.3	500	88.0	400	82.9	400	
35.5	400	80.5	300	74.5	300	
29.2	300	61.7	150	63.6	200	
21.2	200	47.1	80.0	47.0	100	
8.3	100	33.1	40.0	27.6	50.0	
-3.6	50.0	20.3	20.0	19.9	21.0	
-14.1	25.0	7.2	10.0	5.0	35.0	
-24.9	10.0					

^{*a*} Boiling temperature at the pressure p.

formed in the experiments given in Tables 2 and 3. The isothermic bomb process and the correction to standard states were calculated following the procedure in ref 65 (see Table 2). The expansion coefficient is estimated to be 10^{-6} (liquids) or 10^{-7} K⁻¹ (solids), and the other auxiliary data are given in Table 3. The specific heats of combustion (Δu_c) obtained from all successful combustion experiments are listed in Table 2. The standard enthalpies of combustion (ΔH_c°) and the standard heats of formation (ΔH_f°) are calculated thereof (see Table 5). The standard deviation given results from all standard deviations of all data applied, including the contribution of the applied auxiliary compounds (Table 4, footnote *f*).

The heats of sublimation and the heats of vaporization are calculated

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from the equilibrium vapor pressure p at different temperatures (Tables 6 and 7) using the Clausius-Clapeyron relation.

The flow method^{64,66} was used to measure p of 3, 4, 6, and 10. Nitrogen of the volume V with a slow flow v passes the tube, which contains a sample of the substance and which is heated to the temperature T_{sat} . The nitrogen is cooled down in a trap to T_{cond} , and the mass m_{sub} of the condensed product is determined by GC after addition of a certain amount of an internal standard. The saturation pressure p is calculated from m_{sub} and the vapor pressure at T_{cond} .⁶⁶ The obtained values are listed in Table 6.

The vapor pressure of 7-9 was measured by DSC. The probe head of the DSC-2 (Perkin-Elmer) was modified somewhat to evacuate the system. A cover was connected to a vacuum line, and a pressure of 10-1000 mbar can be applied. A sample of the compound (2-5 mg)is sealed in a standard capsule, which contains a lid with a hole of about 0.2 mm diameter. Under constant pressure p, the sample is heated (5 K/min), and a sharp peak is detected when the boiling point is reached. The boiling temperature T is determined from the intercept of the tangent at the increasing side of the signal with the base line. The vapor pressure p obtained at the temperature T is listed in Table 7.

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