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

H.-D. Beckhaus,[†] C. Rüchardt,*[,†] S. I. Kozhushkov,[‡] V. N. Belov,[‡] S. P. Verevkin,[†] and A. de Meijere*[,‡]

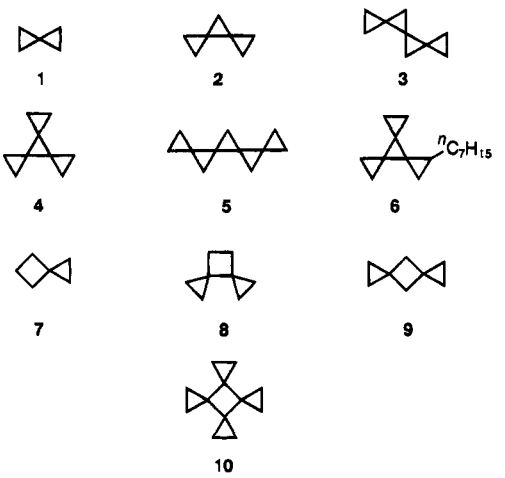
Contribution from the Institut für Organische Chemie und Biochemie der Albert-Ludwigs-Universität Freiburg, Albertstrasse 21, D-79104 Freiburg, Germany, and Institut für Organische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 2, D-37077 Göttingen, Germany

Received July 3, 1995[⊗]

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 from 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 ΔSE = 2.4 ± 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 strain[1] 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, $\Delta H_f°(g)$, 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 rings[5]), 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]rotane[8] and **10** is [4]rotane. It has only been during the past 25 years that synthetic approaches to polyspiranes **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



[†] Albert-Ludwigs-Universität Freiburg.

[‡] Georg-August-Universität Göttingen.

[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1995.

(1) (a) von Baeyer, A. *Chem. Ber.* **1885**, *18*, 2269−2281. (b) Huisgen, R. *Angew. Chem.* **1986**, *98*, 297−311; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 297−311. (c) Wiberg, K. B. *Angew. Chem.* **1986**, *98*, 312−322; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312−322.

(2) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules;* Organic Chemistry Series 38; Academic Press: New York, 1978.

(3) (a) Cremer, D.; Kraka, E. In *Structure and Reactivity*; Liebman, J. F., Greenberg, A., Eds.; VCH: Weinheim, 1988; pp 65−138 and references cited therein. (b) Cremer, D. *Tetrahedron* **1988**, *44*, 7427−7454.

(4) Gustavson, G. *J. Prakt. Chem.* **1896**, *54*, 97−107.

(5) For the explanation of this nomenclature, see: Zefirov, N. S.; Kozhushkov, S. I.; Kuznetsova, T. S.; Kokoreva, O. V.; Lukin, K. A.; Ugrak, B. I.; Tratch, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 7702−7707.

(6) For a recent review, see: de Meijere, A.; Kozhushkov, S. In *Advances in Strain in Organic Chemistry;* Halton, B., Ed.; JAI Press Ltd.: London 1995; Vol. 4, pp 225−282.

(7) For the explanation of this nomenclature see: Ripoll, J. L.; Limasset, J. C.; Conia, J.-M. *Tetrahedron* **1971**, *27*, 2431−2452.

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

(9) See ref 6 and references cited therein.

(10) McGreer, D. E. *Can. J. Chem.* **1960**, *38*, 1638−1639.

(11) Hemmersbach, P.; Klessinger, M. *Tetrahedron* **1980**, *36*, 1337−1343.

(12) (a) Applequist, D. E.; Landgrebe, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 1543−1549. (b) Dzhemilev, U. M.; Dokichev, V. A.; Sultanov, S. Z.; Khusnutdinov, R. I.; Tomilov, Yu. V.; Nefedov, O. M.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 1861−1869; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1989**, 1707−1714.

(13) Denis, J. M.; Le Perchec, P.; Conia, J.-M. *Tetrahedron* **1977**, *33*, 399−408.

(14) (a) Binger, P. *Angew. Chem.* **1972**, *84*, 483; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 433. (b) Doyle, M. J.; McMeeking, J.; Binger, P. *J. Chem. Soc., Chem. Commun.* **1976**, 376−377.

(15) Binger, P.; Doyle, M. J.; Benn, R. *Chem. Ber.* **1983**, *116*, 1−10 and references cited therein.

(16) (a) Fitjer, L. *Chem. Ber.* **1982**, *115*, 1047−1060. (b) Fitjer, L.; Wehle, D. *Chem. Ber.* **1982**, *115*, 1061−1069 and references cited therein.

(17) Conia, J.-M.; Denis, J. M. *Tetrahedron Lett.* **1969**, 3545−3546.

(18) Le Perchec, P.; Conia, J.-M. *Tetrahedron Lett.* **1970**, 1587−1588.

0002-7863/95/1517-11854$09.00/0

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 $\Delta H_f°$(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/mol[30]) based on the same strain-free model[30] lead to an excessive incremental strain energy of ΔSE = 8.9 kcal/mol [65.1 − 2(28.1)]. Apparently, the same excess increment should be applicable n times for a triangulane with n spiro carbon atoms with ΔSE = 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 $\Delta H_f°$(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 PEF404 methods[32] 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]rotane[9] (Scheme 1), namely addition of chloromethylcarbene[48] 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).

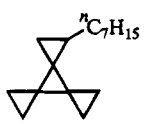
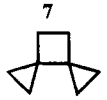
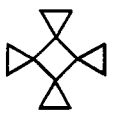
The results of all thermochemical measurements are summarized in Table 1 (for details, see Experimental Section). The new data show that the difference SE − [4SE(C_3H_6)] is equal to 25.7 kcal/mol for **3** and 25.1 kcal/mol for **4**, corresponding to excess increments, ΔSE, of 8.6 and 8.4 kcal/mol per spiro junction, respectively. The experimental value for *n*-heptyl[3]-rotane (**6**), which is less reliable because of incomplete combustion,[50] yields ΔSE = 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.

$$SE = n28.1 + (n - 1)8.6 \qquad \text{[kcal/mol]} \qquad (1)$$

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,

(19) (a) de Meijere, A.; Erden, I.; Weber, W.; Kaufmann, D. *J. Org. Chem.* **1988**, *53*, 152–161. (b) de Meijere, A.; Wenck, H.; Kopf, J. *Tetrahedron* **1988**, *44*, 2427–2438.
(20) Kovacevic, K.; Maksic, Z. B.; Moguš, A. *Croat. Chem. Acta* **1979**, *52*, 249–263.
(21) Boese, R.; Haumann, T.; Kozhushkov, S. I.; de Meijere, A. *Acta Crystallogr.*, to be submitted.
(22) Mekenyan, O.; Bonchev, D.; Balaban, A. T. *J. Comput. Chem.* **1984**, *5*, 629–639.
(23) Ioffe, A. I.; Svyatkin, V. A.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 801–807; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1987**, 727–733.
(24) Maksic, Z. B. In *Theoretical Models of Chemical Bonding*; Part 2, Maksic, Z. B., Ed.; Springer: Berlin, 1990, p.137 ff.
(25) (a) Pascard, C.; Prangé, T.; de Meijere, A.; Weber, W.; Barnier, J.-P.; Conia, J.-M. *J. Chem. Soc., Chem. Commun.* **1979**, 425–426. (b) Prangé, T.; Pascard, C.; de Meijere, A.; Behrens, U.; Barnier, J.-P.; Conia, J.-M. *Nouv. J. Chim.* **1980**, *4*, 321–327. (c) Almenningen, A.; Bastiansen, O.; Cyvin, B. N.; Cyvin, S.; Fernholt, L.; Rømming, C. *Acta Chem. Scand.* **1984**, *A38*, 31–39.
(26) Randic, M.; Kumar, L. *J. Mol. Struct.* **1975**, *26*, 145–161.
(27) Gleiter, R.; Haider, R.; Conia, J.-M.; Barnier, J.-P.; de Meijere, A.; Weber, W. *J. Chem. Soc., Chem. Commun.* **1979**, 130–132.
(28) (a) Humphrey, G. L.; Spitzer, R. *J. Chem. Phys.* **1950**, *18*, 902. (b) Fraser, F. M.; Prosen, E. J. *J. Res. Nat. Bur. Stand.* **1955**, *54*, 143–148.
(29) (a) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1294–1301. (b) Baird, N. C.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1967**, *89*, 3966–3970.
(30) (a) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377–2386. (b) Würthwein, E.-U.; Chandrasekhar, J.; Jemmis, D. E.; Schleyer, P. v. R. *Tetrahedron Lett.* **1981**, *22*, 843–846.
(31) Luk'yanova, V. A.; Pimenova, S. M.; Kolesov, V. P.; Kuznetsova, T. S.; Kokoreva, O. V.; Kozhushkov, S. I.; Zefirov, N. S. *Zh. Fiz. Khim.* **1993**, *67*, 1145–1148; *Russ. J. Phys. Chem.* **1993**, *67*, 1023–1025.
(32) Rasmussen, K.; Tosi, C. *J. Mol. Struct.: THEOCHEM* **1985**, *121*, 233–246.
(33) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds;* Chapman and Hall: London, 1986.
(34) Osawa, E.; Szalontai, G.; Tsurumoto, A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1209–1216.
(35) Dodziuk, H. *Bull. Pol. Acad. Sci. Chem.* **1986**, *34*, 49–51.
(36) Aped, P.; Allinger, N. L. *J. Am. Chem. Soc.* **1992**, *114*, 1–16.
(37) Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H.-W.; Boese, R. *Chem. Ber.* **1991**, *124*, 2499–2521.
(38) Zil'berg, S. P.; Ioffe, A. I.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 261–264; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1983**, 228–231.
(39) Srinivas, G. N.; Radhakrishnan, T. P. *J. Mol. Struct.* **1991**, *246*, 289–300.
(40) Kao, J.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 760–767.
(41) Wiberg, K. B. *J. Org. Chem.* **1985**, *50*, 5285–5291.
(42) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985–1012.
(43) (a) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968. (b) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279–324.
(44) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317–323.
(45) (a) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 5059–5061. (b) Disch, R. L.; Schulman, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 2102–2105.
(46) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127–8134.
(47) de Meijere, A.; Kozhushkov, S. I.; Zefirov, N. S. *Synthesis* **1993**, 681–683.
(48) Arora, S.; Binger, P. *Synthesis* **1974**, 801–803.
(49) (a) Kottwitz, J.; Vorbrüggen, H. *Synthesis* **1975**, 636–637. (b) Review, see: Tomilov, Yu. V.; Dokichev, V. A.; Dzhemilev, U. M.; Nefedov, O. M. *Usp. Khim.* **1993**, *62*, 847–886; *Russ. Chem. Rev.* **1993**, *62*, 799–838.
(50) While compounds **3** and 4 burned completely without any problem, some soot was observed in the combustion of the *n*-heptyl[3]rotane. This is always an indication of incomplete combustion.

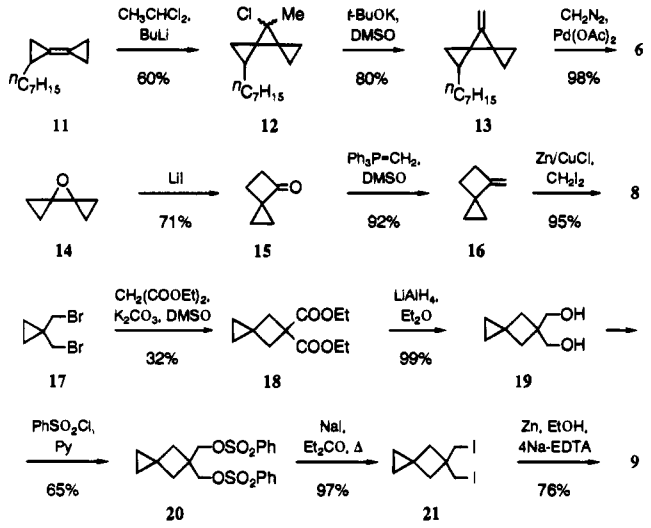
Table 1. Comparison of Thermochemical Data for **1**−**10** According to Theoretical and Experimental Investigations (All Values in kcal/mol)

compound	method	$\Delta H_f°$(g)	SE	ref
 C_3H_6	expt	12.74	28.13[e]	30, 33
 C_4H_8	expt	6.38	26.90[e]	30, 33
	MM2	43.96	63.61	34
	MM2	43.97		35
1	MM2	43.96	63.3,[a] 64.0,[b] 63.31[d]	23
	MM2	44.34		36
	MM3	43.83		37
	MM3	44.15		36
	MM/2ER W	44.45		56
	MINDO/3	28.7	45.6[a]	29, 38
	SR	44.0		39
	SCF MO	58.0	75.2	29b
	STO-3G	43.8	63.7[b]	40
	3-21G	48.60		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		5
	MINDO/3		69.9[a]	38
2	expt	72.27 ± 0.83	98.52 ± 0.83[e]	31
	MM2	107.97	136.2,[a] 137.5[d]	23
	MM2	111.2	142.0[e]	this work
	MM3	102.3	133.1[e]	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
	MM2	109.19	137.1,[a] 139.3,[b] 138.38[d]	23
	MM2	109.2	140.0[e]	this work
	MM3	101.2	132.0[e]	this work
	MINDO3		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
	MMX 88	139.85		5
	expt	129.83 ± 1.62[f]	166.94 ± 1.62[e]	31
5				
 $^nC_7H_{15}$	MM2	68.71	138.44[e]	this work
	MM3	62.34	132.08[e]	this work
	expt	64.99 ± 0.69	134.7 ± 0.69[e]	this work
6				
	MM2	29.71		35
	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				
	expt	52.41 ± 0.31	83.75 ± 0.31[e]	this work
9				
	MM2	85.29	125.0,[a] 125.4,[b] 122.9[d]	23
	MM2	85.30	127.54[e]	this work
	MM3	178.7	220.94[e]	this work
	MINDO/2		143	13
10	expt	106.61 ± 0.49	148.85 ± 0.49[e]	this work

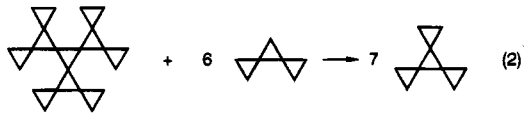
[a] GI method according to Benson.[43] [b] "Homodesmotic" BE method according to George.[44,45] [c] GI method according to Wiberg.[41,42] [d] BE method according to Allinger.[46] [e] GI method according to Schleyer.[30] [f] A mixture of *meso*-**5** and (*d,l*)-**5** was used in the combustion.

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 $\Delta H_f°$(g) is 274.2 kcal/mol, and the isodesmic ring separation reaction with methane that leads to separated rings[52] in its modification for spiro compounds[40] affords ΔH°_{RS} = 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 $\Delta H_f°(g)$



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 $\Delta H_f°(g)$ 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.

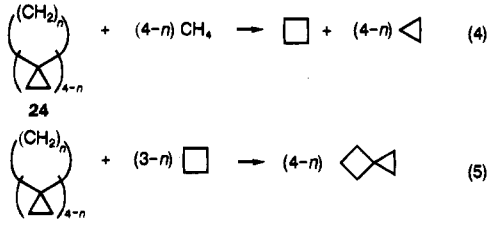
With respect to the thermochemical properties of spirocyclopropanated cyclobutanes, it is remarkable that MM2 calculations yield a $\Delta H_f°(g)$ value for spiro[2.3]hexane (**7**) which is almost identical with the experimental one (29.71[35] *vs* 29.93 kcal/mol). But neither the MM2 nor the MM3 force 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 $\Delta H_f°(g)$ for [*n*]Triangulanes ($n = 1-3$) with Calculated $\Delta H°_{RS}$ Using the Ring Separation Reaction 3 (All Values in kcal/mol)[a]

Compound	1 (*n*=1)	2 (*n*=2)	3 (*n*=3)	4
$\Delta H°_{RS}$	43.37	74.0	104.63	104.63
$\Delta H°_f(g)_{exp.}$	44.23	72.27	106.57	105.91

[a] Calculated with $\Delta H_f°(g) = 12.74$ for C_3H_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 $\Delta H°_{RS}$ and $\Delta H_f°(g)$ (All Values in kcal/mol)[a]



Compound	7 (*n*=3)	8 (*n*=2)	9 (*n*=2)	10 (*n*=0)
$\Delta H°_{RS}$	37.01	67.64	67.64	128.9
$\Delta H°_{calc.}$	-	53.48	53.48	100.58
$\Delta H°_f(g)_{exp.}$	29.93	53.0	52.41	106.61

[a] Calculated with $\Delta H_f°(g) = 6.38$ for C_4H_8; −17.89 for CH_4; 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 $\Delta H_f°(g)$ for [4]rotane (**10**).

The other important question is the excess incremental strain contribution (ΔSE) 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 (ΔSE(**7**) = 0.8 ± 0.4, ΔSE(**8**) = 0.6 ± 0.2, and ΔSE(**9**) = 0.3 ± 0.3 kcal/mol), but for **10**, this destabilizing effect is significant, with ΔSE = 2.4 ± 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 cyclobutane[56] 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 planarization[57] 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.

(51) Kozhushkov, S. I.; Haumann, T.; Boese, R.; de Meijere, A. *Angew. Chem.* **1993**, *105*, 426−429; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 401−403.

(52) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773−778.

(53) Flowers, M. C.; Frey, H. M. *J. Chem. Soc.* **1961**, 5550−5551.

(54) (a) Kybett, B. D.; Carroll, S.; Natalis, P.; Bonnell, D. W.; Margrave, J. L.; Franklin, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 626. (b) Kirklin, D. R.; Churney, K. L.; Domalski, E. S. *J. Chem. Thermodyn.* **1989**, *21*, 1105−1113.

(55) Eaton, P. E. *Angew. Chem.* **1992**, *104*, 1447−1462; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421−1436.

(56) Egawa, T.; Fukuyama, T.; Yamamoto, S.; Takabayashi, F.; Kambara, H.; Ueda, T.; Kuchitsu, K. *J. Chem. Phys.* **1987**, *86*, 6018−6026.

(57) The puckering angle α in spiro[2.3]hexane (**7**) in the crystal[21] is 21°, i.e., slightly smaller than that in cyclobutane, with α = 27.5°.[56] 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 × 8.2 mm column), followed by distillation over 4 Å molecular sieves. The purity (≥99.95%) was checked by GC and DSC analyses. ^{1}H and ^{13}C NMR spectra (with additional DEPT) were recorded in $CDCl_3$ at 250 and 62.9 MHz, respectively; coupling constants (*J*) are given in hertz. ^{1}H NMR spectra for compounds **3**, **4**,[9] **7**,[12] **8**, **9**,[13] and **10**[13,17,19b] and their synthetic precursors **14**[19a] and **15**[13] have been reported. ^{13}C NMR for **7**, δ 17.07 (CH_2), 12.09, 30.82 (2 CH_2), 19.93 (C); **8**, δ 8.87, 27.68 (CH_2), 24.59 (C); **9**, δ 12.40, 39.71 (CH_2), 15.38 (C); **10**, δ 6.02 (CH_2), 28.73 (C); **14**, δ 3.17 (CH_2), 60.48 (C); **15**, δ 16.28 (2 CH_2), 20.48, 43.75 (CH_2), 39.51, 215.06 (C); and **17**, δ 17.75, 40.58 (CH_2), 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 Et_2O (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 H_2O, and the aqueous layer was extracted with Et_2O (100 mL). The combined organic layers were dried over $MgSO_4$, 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); ^{1}H 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 (CH_2), 14.13, 23.77, 23.96 (CH_3), 20.47, 20.86 (CH), 24.88, 29.95, 49.97, 50.10 (C); MS (CI/NH_3) calcd for $C_{15}H_{29}ClN$ (MNH_4^+) 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 H_2O. The aqueous layer was extracted with pentane (3 × 50 mL); the combined organic extracts were washed with H_2O (3 × 50 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Vacuum distillation gave 7.03 g (80%) of **13**: bp 83−85 °C (1 mmHg); ^{1}H 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); ^{13}C NMR δ 7.95, 8.79, 15.72, 22.75, 29.47, 29.55, 29.60, 31.76, 31.98, 93.18 (CH_2), 14.16 (CH_3), 23.43 (CH), 14.59, 19.66, 142.63 (C); MS (CI/NH_3) calcd for $C_{15}H_{28}N$ (MNH_4^+) 222; found 222.

1-*n*-Heptyltrispiro[2.0.2.0.2.0]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 Et_2O (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 H_2O (300 mL) at −5 °C as a solution in 300 mL of Et_2O) 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); ^{1}H 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 = 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); ^{13}C NMR δ 4.06, 4.47, 4.67, 4.79, 10.97, 22.76, 29.46, 29.60, 29.72, 31.92, 32.0 (CH_2), 18.93 (CH), 14.20 (CH_3), 17.52, 18.73, 22.51 (C). Anal. Calcd for $C_{16}H_{26}$: 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 H_2O (2 × 10 mL), and dried over 4 Å molecular sieves to give 10.12 g (92%) of **16**, which contained about 5% of C_6H_6 (GC-NMR data): ^{1}H 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); ^{13}C NMR δ 15.71 (2 CH_2), 27.05, 28.28, 97.66 (CH_2), 27.27, 158.15 (C).

Dispiro[2.0.2.2]octane (8) was obtained using the modified Simmons−Smith procedure[59] (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 CH_2I_2 (53.53 g, 16.1 mL, 0.20 mol) in Et_2O (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-dicarboxylate[60] with $LiAlH_4$ 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 K_2CO_3 (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 H_2O and extracted with Et_2O (3 × 200 mL). The combined etherial solutions were washed with water (3 × 300 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Vacuum distillation afforded 35.29 g (32%) of **18**: bp 113−115 °C (1 mmHg); ^{1}H 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); ^{13}C NMR δ 13.78 (CH_3), 11.46, 37.12, 61.07 (CH_2), 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(hydroxymethyl)spirohexane (19). To a stirred solution of $LiAlH_4$ (4.67 g, 0.123 mol) in Et_2O (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 Na_2SO_4 solution, and filtered. The precipitate was additionally extracted with Et_2O 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**: ^{1}H NMR δ 0.35 (s, 4 H), 1.80 (s, 4 H), 3.50 (s, 2 H), 3.73 (s, 4 H); ^{13}C NMR δ 11.85, 35.43, 69.46 (CH_2), 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); ^{1}H 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); ^{13}C NMR δ 11.33, 34.76, 71.98 (CH_2), 127.75, 129.25, 133.85 (CH), 14.10, 37.76, 135.48 (C). Anal. Calcd for $C_{20}H_{22}O_6S_2$: 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 Et_2CO (200 mL) was refluxed overnight, poured into ice-cold H_2O (500 mL), and extracted with pentane (3 × 100 mL). The combined extracts were washed with water, 5% $Na_2S_2O_3$, and brine and dried over $MgSO_4$. The concentration under reduced pressure afforded 23.21 g (97%) of **21**: ^{1}H NMR δ 0.47 (s, 4 H), 2.03 (s, 4 H), 3.60 (s, 4 H); ^{13}C NMR δ 11.38, 21.88, 39.93 (CH_2), 10.96, 39.70 (C). This substance was used without purification.

(58) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128−1129.

(59) Rawson, R. J.; Harrison, I. T. *J. Org. Chem.* **1970**, *35*, 2057−2058.

(60) Zefirov, N. S.; Kozhushkov, S. I.; Kuznetsova, T. S.; Surmina, L. I.; Raschupkina, Z. A. *Zh. Org. Khim.* **1983**, *19*, 541−548; *J. Org. Chem. USSR* **1983**, *19*, 474−480.

(61) Shubert, W. M.; Leahy, S. M. *J. Am. Chem. Soc.* **1957**, *79*, 381−385.

Table 2. Specific Energies of Combustion (Δu_c) Resulting from All Combustion Experiments (cal/g)

	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]	0.87	1.02	0.92	0.77	0.84	0.81	1.08
c_p (cal/g·K)[b]	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_{sub} (mg)	146.114	29.911	29.260	339.787	328.371	345.443	35.941
m_{cotton} (mg)	0.893	0.651	0.650	1.123	0.844	0.948	0.599
m_{oil} (mg)	167.721						
m_{pe} (mg)	572.115			288.344	275.312	272.383	
m_{Mylar} (mg)		11.254	12.429				9.868
ΔT_c (K)[b]	1.639 09	1.142 50	1.126 68	1.171 43	1.118 48	1.216 70	1.279 88
$\epsilon_{calor}\,\Delta T_c$ (cal)[c]	9828.29	398.970	396.897	7027.06	6709.44	7298.65	451.138
$\epsilon_{cont}\Delta T_c$ (cal)[d]	5.72	0.729	0.727	3.88	3.69	5.01	0.827
$\Delta E_{corr}\Delta T_c$ (cal)[e]	3.66	0.191	0.172	2.36	2.34	2.61	0.215
$m_{fuse}\Delta u_c$(cotton) (cal)[f]	−3.62	−2.64	−2.63	−4.55	−3.42	−3.65	−2.43
$m_{oil}\Delta u_c$(oil) (cal)[f]	1843.83						
$m_{pe}\Delta u_c$(pe) (cal)[f]	6340.98			3195.83	3051.39	3097.39	
$m_{Mylar}\Delta u_c$(Mylar) (cal)[f]		−61.429	−67.842				−53.826
Δu_c(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 °C, T_f = 24.99–25.01 °C; V_{bomb} = 0.046 (micro) or 0.2664 L (macro); p^i_{gas} = 30.00 atm (30.40 bar) at 25.0 °C; $m^i_{H_2O}$ = 0.23 (micro) or 0.78 g (macro); E_{ign} = 0.36 (micro) or 0.35 cal (macro); $m_{platinum}$ = 2.5 (micro) or 4.7 (macro). [b] $\Delta T_c = T_f - T_i + \Delta T_{corr.}$ [c] ϵ_{calor} = 25 088.10 ± 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] $\epsilon_{cont}\,\Delta T_c = \epsilon^i_{cont}\,(T_i - T_h) + \epsilon^f_{cont}\,(T_h - T_f + \Delta T_{corr})$. [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 H_2O], 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 H_2O (500 mL), and extracted with pentane (3 × 100 mL). The combined extracts were washed with water, saturated aqueous NH_4Cl solution, and brine and then dried over $MgSO_4$. 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 microcalorimeter[62] 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 (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

Table 5. Molar Enthalpies of the Crystalline (c) and Liquid (l) Compounds[a] (kcal/mol)

	$\Delta H_c°$(c)[b]	$\Delta H_c°$(l)[b]	$\Delta H_f°$(c)[c]	$\Delta H_f°$(l)[c]	ΔH_{sub}[d]	ΔH_{vap}[d]	ΔH_{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 $\Delta H_c°$(l 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. [g] Melting point, 121.7 °C.

(62) Beckhaus, H.-D.; Rüchardt, C.; Smisek, M. *Thermochim. Acta* **1984**, *79*, 149.

(63) Sunner, S. In *Experimental Chemical Thermodynamics*; Sunner, S., Månsson, M., Eds.; Pergamon Press: Oxford, 1979; Vol. 1, p 13. The calorimeter shown there in Figure 2 was improved by a temperature controlling device of the thermostat bath (±0.001 K).

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

3[b]				**4**[c]			
T_{sat} (°C)	$V(1)$	m_{sub} (mg)	p (Torr)	T_{sat} (°C)	$V(1)$	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_{sat} (°C)	$V(1)$	m_{sub} (mg)	p (Torr)	T_{sat} (°C)	$V(1)$	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] $v = 1.95$ L/h. [c] $v = 1.76$ L/h.

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

7		**8**		**9**	
T (°C)[a]	p (mbar)	T (°C)[a]	p (mbar)	T (°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 ($\Delta H_c°$) and the standard heats of formation ($\Delta H_f°$) 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 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.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (Projekt Me 405/15-3 and Ru 60/29-4) and the Fonds der Chemischen Industrie. We thank BASF, Bayer, Hoechst, Degussa, and Hüls AG for generous gifts of chemicals. The authors are grateful to Dr. B. Knieriem for his careful reading of the manuscript.

JA9521738

(64) Verevkin, S. P.; Beckhaus, H.-D.; Rüchardt, C. *Thermochim. Acta* **1992**, *197*, 27.

(65) Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*; Rossini F. D., Ed.; Vol. 1, Interscience Publisher: New York, 1956; p 75.

(66) (a) Flamm-ter Meer, M. A.; Beckhaus, H.-D.; Rüchardt, C. *Thermochim. Acta* **1984**, *80*, 81. (b) Verevkin, S. P.; Beckhaus, H.-D.; Rüchardt, C. *Thermochim. Acta* **1995**, *249*, 1.