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Thermochemistry and Thermal Decomposition of 9,9′-Bifluorenyl and 9,9′-Dimethyl-9,9′-bifluorenyl – The Stabilization Energy of 9-Fluorenyl Radicals

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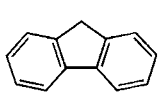
From thermochemical measurements the heats of formation ΔH_f^0(g) for fluorene (**1**), 9-methylfluorene (**2**), 9,9′-bifluorenyl (**5**), and 9,9′-dimethyl-9,9′-bifluorenyl (**6**) were determined. The homolytic cleavage of the dimers **5** and **6** to 9-fluorenyl (**3**) and 9-methyl-9-fluorenyl radicals (**4**), respectively, was studied in mesitylene with thiophenol as trapping agent and found to follow first-order kinetics. The activation parameters $\Delta H^{+}(\mathbf{5}) = 212.6\ (\pm 2.1)$ kJ mol^{-1}, $\Delta S^{+}(\mathbf{5}) = 70.3\ (\pm 4.2)$ J mol^{-1} K^{-1}, $\Delta H^{+}(\mathbf{6}) = 164.9\ (\pm 0.7)$ kJ mol^{-1}, and $\Delta S^{+}(\mathbf{6}) = 88.2\ (\pm 1.9)$ J mol^{-1} K^{-1} were obtained. For **3** and **4** the radical stabilization energies *RSE*(**3**) = 67 (±7) kJ mol^{-1} (relative to isopropyl) and *RSE*(**4**) = 64 (±8) kJ mol^{-1} (relative to *tert*-butyl) were determined by a comparison with the activation parameters of the thermolysis of alkanes possessing the same strain enthalpy. The heats of formation for **3** and **4** and the C–H bond dissociation energies for the C–H bond in the 9-position of **1** and **2** were determined to be $\Delta H_f^0(\mathrm{g},\mathbf{3}) = 300$ kJ mol^{-1}, $\Delta H_f^0(\mathrm{g},\mathbf{4}) = 268$ kJ mol^{-1}, $BDE_{\mathrm{C-H}}(\mathbf{1}) = 343$ and $BDE_{\mathrm{C-H}}(\mathbf{2}) = 338$ kJ mol^{-1} (estimated errors correspond to those of the *RSE* values). A good correlation between the heats of vaporization of 37 aromatic hydrocarbons and their calculated solvent-accessible surfaces was demonstrated. Hence, a new method to estimate heats of vaporization was established.

In the course of our investigation[1,2] of the thermal dissociation of C–C bonds into alkyl radicals according to eq. (1) we found that the enthalpies of activation ΔH^{+} are linearly dependent on the release of strain enthalpy D_s [$D_s = H_s(\mathrm{R-R}) - 2H_s(\mathrm{R\cdot})$] in the course of the dissociation process on the one hand and on the stabilization enthalpies of the radicals being generated, e.g. by resonance, on the other hand. In this way it became possible to determine radical stabilization energies *RSE* from kinetic and thermochemical data[2]. For the series cumyl (*RSE* = 35.2 kJ mol^{-1}), 1,1-diphenylethyl (*RSE* = 46.0 kJ mol^{-1}), and triphenylmethyl (*RSE* = 83.7 kJ mol^{-1})[2,3] it was found that the stabilizing effect of the second and third α-phenyl group is smaller than that of the first one. This was ascribed to the non-planarity of benzhydryl and triphenylmethyl radicals, respectively[2,3].

$$\mathrm{R-R} \xrightarrow{\Delta T} 2\,\mathrm{R\cdot} \qquad (1)$$

In order to test this hypothesis we investigated the thermochemistry of the hydrocarbons fluorene (**1**), 9-methylfluorene (**2**), 9,9′-bifluorenyl (**5**), and 9,9′-dimethyl-9,9′-bifluorenyl (**6**) and studied the thermolysis of **5** and **6** into 9-fluorenyl-type radicals which cannot deviate from planarity because of their rigid structures.

From these data the heats of formation ΔH_f^0(g) and the radical stabilization enthalpies *RSE* of the radicals fluorenyl (**3**) and 9-methylfluorenyl (**4**) were obtained and the C–H bond dissociation enthalpies in the 9-position of **1** and **2** were calculated and compared with results in the literature. Similar work for 9-hydroanthryl-, 9-xanthyl-, and 9,9-dimethyl-10-anthryl radicals will be reported independently[4].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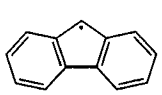
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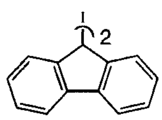

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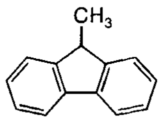

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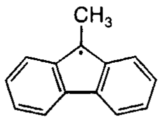

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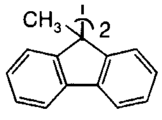

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Synthesis

The commercially available fluorene[5] (**1**) contained about 5% of an unidentified impurity, detected by GC. Purification was achieved by repeated recrystallization from ethanol. Compounds **2**, **5**, and **6** were synthesized by known methods[6,9] and purified by crystallization. Compounds **1** and **2** were, in addition, sublimed to remove traces of solvents. In the samples of **1**, **2**, and **5** no impurities (>0.001%)

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could be detected by GC. DSC measurements of the melting process[10] established a purity of >99.99%. The thermolabile dimer **6** decomposed at its melting point and could not be analyzed by GC without decomposition. Its purity was checked by HPLC and found to be at least 99.9%.

Thermochemistry

The combustion experiments with pellets of the crystalline samples were performed in an isoperibolic calorimeter with a stirred water bath[11], partly using paraffin oil as auxiliary material. The detailed results are summarized in Table 4 of the experimental section. The standard heats of formation $\Delta H_f^\circ(c)$ are listed in Table 1. From an earlier investigation of the combustion of fluorene (**1**) of lower purity ($\cong$ 99%)[12] a value of $\Delta H_f^\circ(\mathbf{1},c) = 89.1 \pm 4.1$ kJ mol^{-1} had been reported[13]. Our new result for $\Delta H_f^\circ(\mathbf{1},c) = 89.87 \pm 1.40$ kJ mol^{-1} (Table 1), due to its smaller percentage error, increases the precision of this important value. The heats of formation $\Delta H_f^\circ(c)$ of **2** (65.25 ± 1.02 kJ mol^{-1}), **5** (197.48 ± 1.94 kJ mol^{-1}), and **6** (203.96 ± 2.01 kJ mol^{-1}) have been determined for the first time. They show a comparable small percentage error as obtained for **1**.

Table 1. Thermodynamic data for fluorene (**1**), 9-methylfluorene (**2**), 9,9′-bifluorenyl (**5**), and 9,9′-dimethyl-9,9′-bifluorenyl (**6**) for the condensed phase and for the gas phase. All values in [kJ mol^{-1}][a]

	ΔH°_c (c)	ΔH°_f (c)	$\Delta H_{m,T}$ [b]	$\Delta H_{v,T}$ [c]	$\Delta H^\circ_{sub,T}$	T_{sub} [K][d]	ΔH°_{sub} $_{298K}$ [e]	ΔH°_f (g) [f]
1	-6634.63	89.87	19.46	65.67	84.85	323-	85.13	175.00
	(± 1.08)	(± 1.40)			(± 0.42)	363		(± 1.46)
2	-7289.36	65.25	16.32	66.44	82.76 [g]	318-	82.77	148.01
	(± 0.25)	(± 1.02)			(± 0.29)	358		(± 1.06)
5	-13001.19	197.48	36.90	95.71	131.75	383-	132.61	330.09
	(± 0.76)	(± 1.94)			(± 1.13)	408		(± 2.25)
6	-14366.73	203.96	≈25.1[h]	≈94.6	118.66	368-	119.74	323.70
	(± 0.41)	(± 2.01)		[i]	(± 1.34)	403		(± 2.42)

[a] Standard deviations in brackets. – [b] DSC measurements. – [c] $\Delta H_{v,T} = \Delta H^0_{sub,298K} - \Delta H_{m,T}$. – [d] Temperature interval at which the equilibrium vapor pressures were measured. – [e] Extrapolated values of $\Delta H^0_{sub,T}$ (T = average temperature of the determination) up to 298 K with Cp(c) of DSC measurements (Table 8) and Cp(g) of MM3 force-field calculations (Table 8). – [f] Standard deviations calculated from the standard deviations of ΔH^0_f(c) and $\Delta H^0_{sub,T}$. – [g] Value calculated from measured $\Delta H_{v,T}$ and ΔH_m (m.p. = 45°C). – [h] Substance melts with slight decomposition. – [i] $\Delta H_{v,T} = \Delta H^0_{sub,298k} - \Delta H_{m,T}$.

The *enthalpies of fusion* of **1**, **2**, and **5** were determined by a power-compensated DSC calorimeter (Table 1). The result for **1**, 19.46 kJ mol^{-1}, is in good agreement with a value reported in the literature[14] (19.58 kJ mol^{-1}).

The *enthalpies of sublimation* of compounds **1**, **2**, **5**, and **6** were determined from their equilibrium vapor pressures, measured by the amount of the gaseous compounds being transported[15,16] in a nitrogen stream which was saturated over finely powdered material at constant temperature. The apparent vapor pressure p' was calculated from the amount of condensed material which was collected within a definite time, measured by GC and the residual vapor pressure at the condensation temperature[17]. From the linear correlation between p' and $1/T$ the enthalpy of sublimation $\Delta H^\circ_{sub,T}$ at the temperature T was obtained. The sublimation enthalpies $\Delta H^\circ_{sub,T}$ are compiled in Tables 1 and 6 (see Experimental). Because of the high temperatures of measurement [$T_{average}$ = 343 (**1**), 338 (**2**), 395 (**5**), 385 K (**6**)] they had to be corrected to the standard temperature 298 K. The molar heat capacities Cp for the crystalline state at 298 K and at $T_{average}$ were measured by DSC (Table 7) and those for the gas phase were estimated from force-field calculations (Table 7). From these data the ΔH°_{sub} values in Table 1 were calculated, assuming a mean value of Cp within the temperature interval. The same procedure, based on force-field calculations, had been successfully used to calculate the temperature dependence of ΔH°_{sub} of several alkylated benzenes[3]. Several values for the enthalpy of sublimation extrapolated to 298 K had been reported for fluorene (**1**) (82.8[18], 80.3 ± 0.8[19], 81.8[20], 83.1 ± 1.3[21], and 80.21 ± 0.17 kJ mol^{-1}[13]), and they are in reasonable agreement with our value of 85.13 ± 0.42 kJ mol^{-1}.

The strain enthalpies H_s for fluorene and its derivatives depend on the definition of the strainfree reference ΔH_f^N for these compounds. Such a definition is somewhat arbitrary, because the parent compound **1** itself is not strainfree due to the five-membered ring. In order to avoid establishing a scale for H_s throughout this work, only relative values are used, namely the strain-free dissociation enthalpy D'_s which has been defined previously as $D'_s = H_s(R-R) - 2\,H_s(RH)$[2]. Values of D'_s are listed in Table 3 and discussed below.

The structure of the preferred conformation of the dimers **5** and **6** has been calculated by MM2 and MM3. Both adopt *gauche* conformations (see Figure 1) with torsional angles H–C–C–H = 69.88° (**5**) and $CH_3-C-C-CH_3$ = 76.18° (**6**). The central C–C bond of **5** (1.534 Å) is shorter than in **6** (1.559 Å). This elongation illustrates the higher strain in the C_q-C_q-ethane **6** compared to the C_t-C_t-ethane **5** (see Table 3)[22].

The *gauche* structures explain the unexpected low heats of vaporization ΔH_v of **5** and **6** (see Table 1). From simple group additivity schemes[23] for the heats of vaporization ΔH_v, it would be expected that ΔH_v of the dimers **5** and **6** was about twice as high as ΔH_v of the monomers **1** and **2**. For both systems of corresponding dimer and monomer (**1** and **5**; **2** and **6**) we found, however, a non-additivity (i.e. ΔH°_v (**5**) = 95.7 kJ mol^{-1} < $2[\Delta H^\circ_v(\mathbf{1})]$ = 65.7 kJ mol^{-1}). Apparently, the group additivity[23] scheme for the estimation of $\Delta H_{v,T}$ is not applicable in this case.

Therefore, a new procedure for the estimation of heats of vaporization was developed. We propose to calculate the surface which is accessible for other molecules, i.e. solvent-accessible surface, as a measure of the intermolecular forces, which control the heat of vaporization. As a test, this specific molecular property was calculated with Connolly's program[24] for a series of aromatics and alkyl-substituted aromatics by using a probe sphere of 250 pm. Figure 2

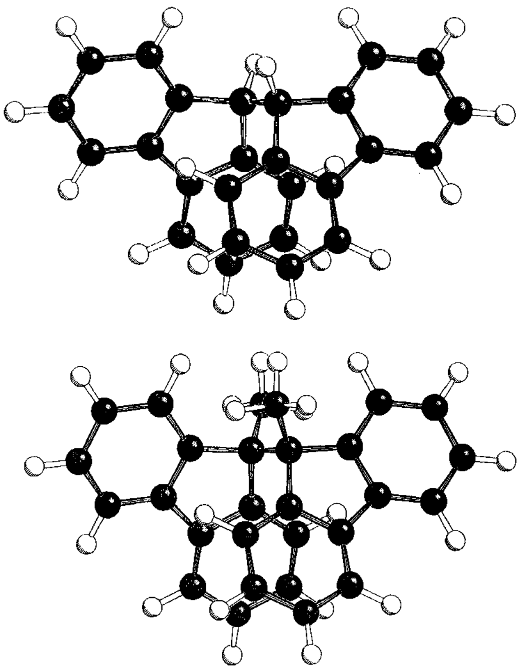

Figure 1. Structures of the dimers **5** and **6** based on force-field calculations

shows that there exists a good correlation between the surface data and the heats of vaporization. This provides a superior way for the estimation of heats of vaporization $\Delta H_{v,T}$ in comparison with the known increment procedures because the solvent-accessible surface represents not only constitutional properties but also conformational properties of a specific structure.

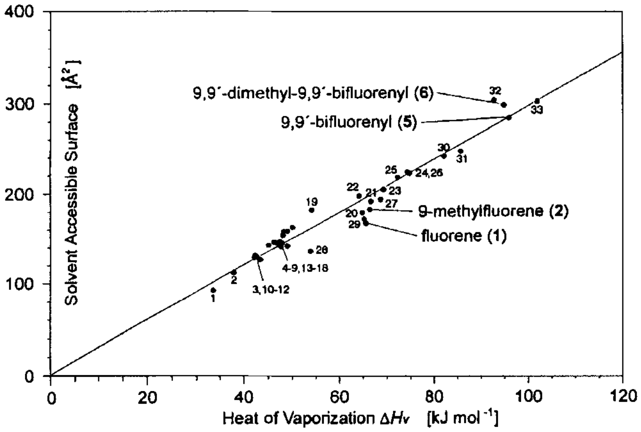

Figure 2. Correlation between the solvent-accessible surface and the heat of vaporization ΔH_v of several alkyl-substituted aromatic hydrocarbons (Table 8)

Kinetics of the Thermolysis of the Dimers 5 and 6

The rate constants for the thermolysis of the dimers **5** and **6** were measured in mesitylene in the presence of a tenfold excess of thiophenol as trapping agent[25] by the ampoule technique. The decrease of the concentration of **5** was followed by GC and of **6** by HPLC. Precise first-order kinetics was observed up to 90% conversion.

Table 2. Rate constants and activation parameters for the thermolytic cleavage of 9,9'-bifluorenyl (**5**) and 9,9'-dimethyl-9,9'-bifluorenyl (**6**) in mesitylene in the presence of thiophenol[a]

5	T [K]	519.6	531.8	543.5	556.4	562.6
[b]	k	0.2190	0.625	2.000	5.71	10.10
	$[10^4 s^{-1}]$	(± 0.0028)	(± 0.016)	(± 0.053)	(± 0.15)	(± 0.10)
6	T [K]	372.9	388.4	395.9	403.7	412.2
[b]	k	0.02498	0.02152	0.5646	1.590	4.352
	$[10^4 s^{-1}]$	(± 7.0 E-4)	(± 1.7 E-3)	(± 0.023)	(± 0.038)	(± 0.064)

	$\Delta G^{\ddagger}$(300 C) [kJ/mol]	$\Delta H^{\ddagger}$ [kJ/mol]	$\Delta S^{\ddagger}$ [e.u.]	$T_{1/2}$ [c] [K]
5	172.4 (± 3.4)	212.6 (± 2.1)	70.3 (± 4.2)	543.3
6	114.4 (± 0.7)	164.9 (± 0.7)	88.2 (± 1.9)	405.5

[a] Standard deviation in brackets. – [b] In mesitylene in the presence of a tenfold excess of thiophenol as trapping agent. – [c] Temperature at half-life of 1 h.

The products were quantitatively analyzed by GC using peak area correction factors with an internal standard. The products were fluorene (**1**) (100%) or 9-methylfluorene (**2**) (30–70%) and 9-methyl-9-fluorenyl phenyl thioether (70–30%), respectively. They were identified by GC–MS analysis and, where possible, by a comparison with the spectra of authentic samples.

The activation parameters (Table 2) were calculated from five kinetic runs over a temperature range of ≥ 40 K. The experimentally determined standard deviations of the rate constants k were used as weighing factors in the correlation calculations of the Eyring equation[26].

Results and Discussion

The dimers of fluorene (**5**) and of 9-methylfluorene (**6**) proved to be of very different thermal stability. Whereas 9,9'-dimethyl-9,9'-bifluorenyl (**6**) decomposes at 132°C with a half-life of one hour, unsubstituted 9,9'-bifluorenyl (**5**) decomposes with the same rate at 270°C (Table 2). A small portion of this large effect could be explained by the different types of radicals which are formed, a secondary radical **3** from **5** versus a tertiary radical **4** from **6**. The larger fraction of the difference, however, must be caused by the different amounts of strain enthalpy D_s, which are released during the dissociations[2].

As an estimate of this strain of dissociation, $D_s = H_s(R-R) - 2H_s(R\cdot)$, we have used previously[2] the strain difference between the dimer and the monomer, $D'_s = H_s(R-R) - 2H_s(RH)$[2]. The values for D'_s are calculated directly from the $\Delta H_f^{\circ}(g)$ values of **1**, **2**, **5**, and **6** and the group increments[27] of those groups which differ in the dimer from the monomer (Table 3, footnote[b]).

The dissociation of dimer **6** is associated with a release of strain enthalpy $D'_s(\mathbf{6}) = 12.12$ kJ mol^{-1}. A positive change of strain is normal for thermal dissociations of C–C bonds. For the thermal dissociation of **5**, in contrast, $D'_s(\mathbf{5}) = -44.75$ kJ mol^{-1}, a decrease of strain D'_s was found.

This is, to our knowledge, the first example of steric deceleration during a bond dissociation process. This unusual behavior may be due to strong attractive forces between the two fluorenyl groups in dimer **5**, which prefers like dimer **6** the *gauche* conformation (Figure 1). The repulsion between the methyl groups in dimer **6** however is responsible for its high strain enthalpy, which exceeds the attractive forces between the aromatic groups.

When the D_s' values are known, the steric effects on the rates of dissociation of the dimers **5** and **6** can be estimated from the reference systems tetraalkylethanes[28] and hexaalkylethanes[29].

$$\Delta G^{\ddagger}_{300}(\text{tetraalkylethanes}) = 277\ (\pm 6)\ \text{kJ mol}^{-1} - 0.77\ (\pm 0.04)\ D_s \quad (2)$$

$$\Delta G^{\ddagger}_{300}(\text{hexaalkylethanes}) = 264\ (\pm 4)\ \text{kJ mol}^{-1} - 0.80\ (\pm 0.05)\ D_s \quad (3)$$

From the established linear correlations between D_s and the rates of dissociation or $\Delta G^{\ddagger}$ (of the tetraalkylethanes or hexaalkylethanes, respectively) at a certain temperature[2] one can calculate the value of $\Delta G^{\ddagger}$ for a reference alkane with a similar D_s value as the dimer in question [$\Delta G^{\ddagger}$ (ref., D_s), see Table 3]. Using the known $\Delta S^{\ddagger}$ of the dimer and the mean value of the reference system[2], we obtained the $\Delta H^{\ddagger}(\text{ref.},D_s)$ values. Correction of the entropy difference $\Delta\Delta S^{\ddagger}$ between the two thermolysis reactions affords the activation enthalpy $\Delta H^{\ddagger}$ (ref., D_s) of an alkane homolysis in which the same amount of strain D_s is released as in the thermolysis of **5** or **6**. These data reflect the steric effect on the dissociation of the dimers. The radical stabilization energy (*RSE*) is then calculated from the difference between the activation enthalpy $\Delta H^{\ddagger}(\text{ref.},D_s)$ and the activation enthalpy of homolysis of the corresponding dimer **5** or **6**.

$$RSE\ (\text{radical}) = 0.5\ [\Delta H^{\ddagger}\ (\text{ref.},\ D_s) - \Delta H^{\ddagger}\ (\text{R}-\text{R})] \quad (4)$$

For radical **3** a $RSE(\mathbf{3}) = 67 \pm 7$ kJ mol^{-1} is obtained relative to a secondary alkylradical e.g. isopropyl and for radical **4** $RSE(\mathbf{4}) = 64 \pm 8$ kJ mol^{-1} relative to a tertiary alkylradical e.g. *tert*-butyl, which are in reasonable agreement.

Radical stabilization energies *RSE* are related to the corresponding C–H bond dissociation energies *BDE*. The most recently determined value for the C–H bond dissociation energies of alkanes are ≈ 410 kJ mol^{-1} for the secondary C–H bond (410[30a], 411 kJ mol^{-1}[30b]) in propane and ≈ 402 kJ mol^{-1} for the tertiary C–H bond (399–405[30a]; 401 kJ mol^{-1}[30b]) in isobutane. These values have been obtained from the critical evaluation of several experimental measurements of two types of reactions, namely C–C bond cleavages and halogene transfer reactions, and they are larger by 10–12 kJ mol^{-1} then those from the older compilation[31].

The C–H bond dissociation energies for fluorene (**1**) and 9-methylfluorene (**2**) can be calculated from the radical stabilization enthalpies *RSE* of the radicals **3** and **4** and the C–H bond dissociation energies of alkanes according to equations (5) and (6).

$$BDE_{\text{C-H}}(\mathbf{1}) = BDE_{\text{C-H}}(\text{propane}) - RSE(\mathbf{3}) \quad (5)$$

$$BDE_{\text{C-H}}(\mathbf{2}) = BDE_{\text{C-H}}(\text{isobutane}) - RSE(\mathbf{4}) \quad (6)$$

The value obtained for fluorene $BDE_{\text{C-H}}(\mathbf{1}) = 343$ kJ mol^{-1} is in good agreement with the literature value (344[32], 333[33a], 335 kJ mol^{-1}[33b]). The value for the tertiary C–H bond dissociation energy for 9-methylfluorene was determined to be $BDE_{\text{C-H}}(\mathbf{2}) = 338$ kJ mol^{-1} (Table 3). The errors of these values are equal to the errors of the *RSE* values given above together with the errors of the reference values $BDE_{\text{C-H}}$(alkane), which were estimated to be about ± 4 kJ mol^{-1}.

The enthalpies of formation of the radicals **3** and **4** were accordingly calculated to be $\Delta H_f^\circ(\text{g},\mathbf{3}) = 300$ and $\Delta H_f^\circ(\text{g},\mathbf{4}) = 268$ kJ mol^{-1} (Table 3).

Table 3. Release of strain energy Ds' for the dissociation of the dimers **5** and **6**, radical stabilization energies *RSE*, bond dissociation energies *BDE* and heats of formation $\Delta H_f^0(\text{g})$ for the gas phase of the radicals 9-fluorenyl (**3**) and 9-methylfluorenyl (**4**)[a]

	D_s' [b]	$\Delta G^{\ddagger}(\text{ref.},D_s')$ [c]	$\Delta H^{\ddagger}(\text{ref.},D_s')$ [c]
5	-44.75	311 (± 6)	347 (± 7)
6	+12.12	254 (± 4)	293 (± 8)

	RSE [d]	$BDE_{C\text{-}H}$ [e],[g]	$\Delta H^\circ_f(\text{g})$ [f],[g]
3	67 (± 7)	343	300
4	64 (± 8)	338	268

[a] The values were calculated from data of thermodynamic and kinetic measurements (Tables 1 and 2, see also text); standard deviations in brackets; all values in [kJ/mol]. – [b] $D_s'(\mathbf{5}) = \Delta H_f^0(\text{g},\mathbf{5}) - 2[\Delta H_f^0(\text{g},\mathbf{1})] - 2\ C_t + 2\ Cs$; $D_s'(\mathbf{6}) = \Delta H_f^0(\text{g},\mathbf{6}) - 2[\Delta H_f^0(\text{g},\mathbf{2})] - 2\ C_q + 2\ C_t$; $C_s = -21.46$ kJ/mol, $C_t = -9.04$ kJ/mol, $C_q = -1.26$ kJ/mol[27]. – [c] Values for the corresponding reference system (tetraalkylethanes or hexaalkylethanes using the D_s' values of [b]; the average values for the entropies are $\Delta S^{\ddagger}$(tetraalkylethanes) = 62 ± 4 and $\Delta S^{\ddagger}$(hexaalkylethanes) = 68 ± 7 kJ/mol. – [d] The values for the radical stabilization energies were calculated by using the $\Delta G^{\ddagger}/D_s'$ correlations for the dissociation of tetraalkylethanes ($\Delta G^{\ddagger}_{300} = 277$ kJ/mol $- 0.77\ D_s'$)[29] and hexaalkylethanes ($\Delta G^{\ddagger}_{300} = 264$ kJ/mol $- 0.80\ D_s'$)[28] and the calculated values D_s' of [b]; $RSE(\mathbf{3}) = [\Delta H^{\ddagger}_{300}(\text{ref.},D_s') - \Delta H^{\ddagger}_{300}(\mathbf{5})]/2$; $RSE(\mathbf{4}) = [\Delta H^{\ddagger}_{300}(\text{ref.},\ D_s') - \Delta H^{\ddagger}_{300}(\mathbf{6})]/2$. – [e] $BDE_{\text{C-H}}(\mathbf{1}) = BDE_{\text{C-H}}(\text{propane}) - RSE(\mathbf{3})$; $BDE_{\text{C-H}}(\mathbf{2}) = BDE_{\text{C-H}}(\text{isobutane}) - RSE(\mathbf{4})$. – [f] $\Delta H_f^0(\text{g,radical}) = \Delta H_f^0(\text{g,monomer}) + BDE_{\text{C-H}}(\text{monomer}) - \Delta H_f^0(\text{H}\cdot)$; $\Delta H_f^0(\text{H}\cdot) = 218.0$ kJ/mol. – [g] Standard errors comparable to those given for *RSE*.

The energy of the transition state of the dissociation corresponds to the sum of $\Delta H_f^\circ(\text{g,dimer})$ (see Table 1) and $\Delta H^{\ddagger}(\text{dimer})$ (see Table 2), namely 543 kJ mol^{-1} for **5** and 489 kJ mol^{-1} for **6**. Due to the principle of microscopic reversibility, the reverse reaction, the recombination of the radicals, passes through the same transition state. The energy level of the two radicals corresponds to twice $\Delta H_f^\circ(\text{g,radical})$ (see Table 3), namely 600 kJ mol^{-1} for **3** and 536 kJ mol^{-1} for **4**. This leads to negative values for the activation enthalpy of recombination of $\Delta H^{\ddagger}_{\text{rec}} = 2\Delta H_f^\circ(\text{g,radical}) - \Delta H^{\ddagger}(\text{dimer}) = -57$ and -47 kJ mol^{-1} for **3** and **4**, respectively. Obviously, the activated complex is stabilized as a result of attractive forces between the radicals. In the dimers strong attractive forces have been deduced from their measured thermochemical stabilites, (see above), leading to a negative strain enthalpy for **5**. A fraction of these strong forces between the fluorenyl moieties seems to persist in the activated complex decreasing its energy compared to the energy of the free radicals.

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Experimental

All compounds were handled in an inert atmosphere (N_2) by using carefully dried glassware and carefully dried solvents. – ^1H NMR: Bruker WM 250 (250 MHz); solvent $CDCl_3$, $CHCl_3$ as internal standard. – GC: Carlo Erba Fraktometer Vega Series GC 6000, Hewlett Packard Integrator 3390A, N_2 flow 2 ml/min, SE-30 capillary columns 25 m. Standard temperature program: 100°C for 5 min; with 10°C/min up to 250°C. – MS: Varian Fraktometer 3700, Finnigan Mat 44s. – HPLC: Waters pump 6000A, Merck-Hitachi UV-Vis detector, Macherey-Nagel column ET 250/8/4 NUCLEOSIL 5C18. – Melting points: Büchi apparatus (Dr. Tottoli), uncorrected. – DSC: Perkin-Elmer DSC-2C with Olivetti PC M 28. – Thermolysis: Lauda constant-temperature chamber NB-315 (oil-filled), thermostated tin bath[34] with Oxford Electronic Instruments control system DTC/CK 01.

Fluorene (**1**) was commercially available[5]. It was recrystallized 25 times from ethanol. An impurity was enriched in the mother liquor with a factor of 2 when 1.5 l of ethanol was used for 100 g of **1**. It was not possible to determine the structure of the impurity by ^1H NMR and MS. To remove traces of solvent, **1** was finally sublimed in vacuo; m.p. 115°C. GC: no impurity $\geq$0.001%.

9-Methylfluorene (**2**)[7]: A solution of 10.0 g (51.0 mmol) of 9-hydroxy-9-methylfluorene[6] in 300 ml of glacial acetic acid was heated for 1 h under reflux. The solution was hydrogenated with a platinum catalyst at standard pressure. The catalyst was removed

Table 4. Combustion calorimetry of fluorene (**1**), 9-methylfluorene (**2**), 9,9′-bifluorenyl (**5**), and 9,9′-dimethyl-9,9′-bifluorenyl (**6**)

	1	2	3	4	5	6
m (**1**) [g] [a]	0.321287	0.298724	0.323819	0.296843	0.281410	0.303655
m_{oil} [g] [a]	0.034435	0.044324	0.040281	0.043213	0.037624	0.038211
m_{cotton} [g] [a]	0.000884	0.000873	0.000991	0.001032	0.001147	0.000970
ΔT_C [K] [b]	0.57398	0.55640	0.58903	0.55170	0.51650	0.55309
ε_{calor} $(-\Delta T_C)$ [J] [c]	-14409.86	-13968.54	-14787.60	-13850.50	-12966.89	-13885.23
ε_{cont} $(-\Delta T_C)$ [J] [c]	-7.61	-7.41	-7.78	-7.36	-6.82	-7.36
ΔE_{corr} [J] [d]	7.78	7.36	7.91	7.28	6.82	7.41
m_{oil} Δu_C [J] [d]	1583.56	2038.36	1852.42	1987.23	1730.21	1757.20
m_{cotton} Δu_C [J] [d]	14.98	14.77	16.78	17.49	19.41	16.44
Δu_C (**1**) [J g^{-1}]	-39869.9	-39882.9	-39889.0	-39901.2	-39855.4	-39881.2
ΔH_C (**1**) [kJ mol^{-1}] [e]	-6633.0	-6635.1	-6636.1	-6638.2	-6630.6	-6634.9
ΔH_f (**1**) [kJ mol^{-1}] [e]	88.2	90.4	91.4	93.4	85.8	90.1

	1	2	3	4	5	6	7
m (**2**) [g] [a]	0.354870	0.354866	0.361160	0.336826	0.356058	0.350855	0.358448
m_{oil} [g] [a]	-	-	-	-	-	-	0.039661
m_{cotton} [g] [a]	0.000944	0.000980	0.000830	0.000996	0.000964	0.000848	0.000839
ΔT_C [K] [b]	0.57184	0.57182	0.58194	0.54277	0.57376	0.56524	0.65006
ε_{calor} $(-\Delta T_C)$ [J] [c]	-14.356.10	-14355.56	-14609.48	-13626.37	-14404.30	-14190.50	-16319.65
ε_{cont} $(-\Delta T_C)$ [J] [c]	-7.62	-7.62	-7.70	-7.16	-7.57	-7.49	-8.62
ΔE_{corr} [J] [d]	7.82	7.82	7.99	7.41	7.87	7.74	8.54
m_{oil} Δu_C [J] [d]	-	-	-	-	-	-	1823.93
m_{cotton} Δu_C [J] [d]	15.98	16.61	14.06	16.86	16.32	14.35	14.22
Δu_C (**2**) [J g^{-1}]	-40404.7	-40401.9	-40407.8	-40400.1	-40404.1	-40399.6	-40396.8
ΔH_C (**2**) [kJ mol^{-1}] [e]	-7289.8	-7289.3	-7290.4	-7289.0	-7289.7	-7288.9	-7288.4
ΔH_f (**2**) [kJ mol^{-1}] [e]	65.7	65.2	66.3	64.9	65.6	64.8	64.3

Table 4 *(Continued)*

	1	2	3	4	5	6
m (**5**) [g] [a]	0.284344	0.293152	0.288563	0.298560	0.292048	0.289136
m_{oil} [g] [a]	0.047133	0.046927	0.044129	0.047109	0.044443	0.047056
m_{cotton} [g] [a]	0.000835	0.000809	0.000865	0.000718	0.000871	0.000826
ΔT_c [K] [b]	0.53216	0.54587	0.53360	0.55451	0.53958	0.53983
ε_{calor} ($-\Delta T_c$) [J] [c]	-13359.93	-13700.13	-13392.06	-13916.90	-13542.23	-13548.50
ε_{cont} ($-\Delta T_c$) [J] [c]	-7.07	-7.24	-7.06	-7.36	-7.16	-7.16
ΔE_{corr} [J] [d]	7.24	7.45	7.28	7.57	7.36	7.36
m_{oil} Δu_c [J] [d]	2167.48	2158.07	2029.37	2166.39	2043.80	2164.01
m_{cotton} Δu_c [J] [d]	14.14	13.68	14.64	12.18	14.77	13.97
Δu_c (**5**) [J g^{-1}]	-39306.8	-39319.9	-39320.3	-39310.9	-39315.3	-39320.2
ΔH_c (**5**) [kJ mol^{-1}] [e]	-12998.3	-13002.6	-13002.7	-12999.6	-13001.1	-13002.7
ΔH_f (**5**) [kJ mol^{-1}] [e]	194.6	198.9	199.0	195.9	197.4	199.0

	1	2	3	4	5	6
m (**6**) [g] [a]	0.294984	0.285489	0.298107	0.282312	0.290027	0.304483
m_{oil} [g] [a]	0.045287	0.052390	0.038575	0.043874	0.048163	0.036416
m_{cotton} [g] [a]	0.000809	0.000895	0.001031	0.000897	0.000899	0.001033
ΔT_c [K] [b]	0.55426	0.55215	0.54703	0.53138	0.55162	0.55324
ε_{calor} ($-\Delta T_c$) [J] [c]	-13910.67	-13857.74	-13729.34	-13336.58	-13844.48	-13855.23
ε_{cont} ($-\Delta T_c$) [J] [c]	-7.36	-7.32	-7.28	-7.07	-7.32	-7.36
ΔE_{corr} [J] [d]	7.24	7.11	7.20	6.90	7.15	-7.32
m_{oil} Δu_c [J] [d]	2082.63	2409.27	1773.97	2017.61	2214.88	1674.69
m_{cotton} Δu_c [J] [d]	15.40	15.15	17.45	15.19	15.23	17.49
Δu_c (**6**) [J g^{-1}]	-40040.5	-400043.8	-40041.1	-40035.3	-40041.5	-40040.3
ΔH_c (**6**) [kJ mol^{-1}] [e]	-14366.4	-14367.6	-14366.6	-14364.5	-14366.7	-14366.3
ΔH_f (**6**) [kJ mol^{-1}] [e]	204.0	205.2	204.2	202.2	204.4	203.9

[a] m: air-reduced masses. – [b] $\Delta T_c = T_f - T_i + \Delta T_{corr}$; T_h = 25°C; V_{bomb} = 0.2664 l; p^i_{gas} = 30.00 atm (30.40 bar); m^i_{water} = 5 g; E_{ignit} = 1.46 J; T_i = 297.5 K; $m_{platinum}$ = 9.763 g. – [c] ε_{calor} = 25088.02 ± 2.18 J/K (±0.0087%) from calibration measurements with benzoic acid; $\varepsilon_{cont}(-\Delta T_c) = \varepsilon^i_{cont}(T^i - 298\ K) + \varepsilon^f_{cont}(298\ K - T^f + \Delta T_{corr})$. – [d] ΔE_{corr}: sum of the items 81–85, 87–90, 93, and 94 reported in ref.[45]; $m_{cotton}\Delta u_c$ and $m_{oil}\Delta u_c$: amounts of heat released by the combustion of the auxiliary compounds. – [e] Average from several measurements, see Table 1

by filtration. The solvent was removed from the filtrate, and the crude product was obtained as an oily residue which was recrystallized several times from methanol. To remove traces of solvent, **2** was finally sublimed in vacuo several times; yield of **2** 6.5 g (70%), m.p. 45°C (ref.[6] 76%, m.p. 46°C). GC: no impurity ≥0.001%. – ^{1}H NMR (CDCl$_3$/250 MHz): δ = 1.58 (d, 3H, J = 7 Hz, CH$_3$), 4.00 (q, 1H, J = 7 Hz, C*H*–CH$_3$), 7.31 (m, 4H, Ar*H*), 7.56 (m, 2H, Ar*H*), 7.82 (m, 2H, Ar*H*). – MS (70 eV), *m/z* (%): 181 (12), 180 (56), 166 (18), 165 (100).

9,9'-Bifluorenyl (**5**)[9]: To a solution of 15.0 g (61.1 mmol) of 9-bromofluorene[35] in 100 ml of diethyl ether was added 32.1 ml (64.2 mmol) of a 2 M methyllithium solution. The solution was poured on ice and the mixture extracted several times with diethyl ether. The combined organic layers were washed with water and dried with MgSO$_4$. The solvent was removed to give the solid crude product which was recrystallized several times from toluene/ethanol (1:1). The finely powdered substance was carefully dried (constancy of weight) in vacuo (0.1 Torr) to remove any traces of solvent; yield of **5** 5.95 g (59%), m.p. 245°C (ref.[9] 98%, m.p. 245–246°C). GC: no impurity ≥ 0.001%. – ^{1}H NMR (CDCl$_3$/250 MHz): δ = 4.60 (s, 2H, –CH–), 6.88–7.31 (m, 12H, Ar*H*), 7.64 (m, 4H, Ar*H*). – MS (70 eV), *m/z* (%): 330 (100), 165 (23).

9,9'-Dimethyl-9,9'-bifluorenyl (**6**)[9]: To a solution of 2.0 g (6.0 mmol) of bifluorenylidene[8] in 100 ml of diethyl ether was added at –10°C 20 ml of a 1.5 M methyllithium solution in hexane (30 mmol). Subsequently, a solution of 1.86 ml of iodomethane (30

Table 5. Densities, heat capacities, and expansion coefficients for **1**, **2**, **5**, and **6** and for the auxiliary compounds oil and cottonthread

Substance	d (293 K) [g cm^{-3}]	Cp (298 K) [Jg^{-1}K^{-1}] [a]	expansion-coefficient [10^{-6} K^{-1}] [d]
1	1.20	1.35	0.1
2	1.20	1.43	0.1
5	1.22	1.29	0.1
6	1.23	1.37	0.1
oil [b]	0.88	0.83	1.0
cottonthread [c]	1.50	1.67	0.1

[a] Determined by three measurements (± 0.008 J g^{-1} K^{-1}). – [b] $CH_{1.94}$; $\Delta u_c^0 = 45987.2$ J g^{-1}. – [c] $CH_{1.1774}O_{0.887}$; $\Delta u_c^0 = -16945.2$ J g^{-1}. – [d] Estimated.

Table 6. Equilibrium vapor pressures of the hydrocarbons **1**, **2**, **5**, and **6** determined by the method of transference

	T [K]	Condensation Product [mg]	N2 [l]	Flow [l (N2) / h]	p' [Torr]
1 [a]	323.0	2.480	26.680	1.490	0.0104
	328.0	1.130	7.760	1.490	0.0163
	332.9	1.720	7.550	1.490	0.0255
	338.0	0.887	2.470	1.490	0.0402
	343.0	1.050	1.820	1.490	0.0645
	348.1	1.020	1.150	1.490	0.0994
	353.0	1.000	0.743	1.490	0.151
	358.1	1.116	0.583	1.490	0.223
	363.1	1.070	0.360	1.490	0.331
2 [a]	318.0	7.040	42.410	1.530	0.0171
	323.0	5.740	22.920	1.500	0.0259
	328.0	1.610	4.455	1.500	0.0373
	333.0	1.760	3.326	1.500	0.0546
	338.0	0.976	1.313	1.500	0.0767
	343.0	1.040	0.987	1.500	0.109
	348.1	0.797	0.537	1.500	0.153
	353.1	0.696	0.338	1.500	0.213
	358.0	0.551	0.200	1.500	0.284
5 [b]	383.1	0.142	246.210	1.600	0.0325 E-3
	388.0	0.129	135.280	1.600	0.0538 E-3
	393.0	0.200	120.430	1.600	0.0937 E-3
	398.0	0.236	84.690	1.600	0.157 E-3
	403.0	0.244	55.310	1.690	0.248 E-3
	408.2	0.283	38.700	1.690	0.412 E-3
6 [b]	368.0	0.113	368.100	1.930	0.0160 E-3
	373.0	0.154	275.200	1.930	0.0290 E-3
	378.0	0.206	235.460	1.930	0.0454 E-3
	383.1	0.244	170.000	1.930	0.0743 E-3
	388.0	0.239	163.200	1.770	0.0760 E-3
	393.6	0.294	125.000	1.760	0.122 E-3
	398.0	0.326	89.800	1.760	0.188 E-3
	403.0	0.199	33.100	1.820	0.311 E-3

[a] Condensation temperature $T_{\mathrm{cond.}} = 243.0$ K. – [b] Condensation temperature $T_{\mathrm{cond.}} = 293.0$ K.

mmol) in 20 ml of diethyl ether was added. The solution was poured on ice and the mixture extracted several times with diethyl ether. The combined organic layers were washed with water and dried with $MgSO_4$. The solvent was removed to give the crude solid product which was recrystallized several times from acetone. The finely powdered substance was carefully dried in vacuo (constancy of weight) to remove any traces of solvent. The yield of **6** was 1.93 g (89%), m.p. 210°C (ref.[9] 95%, m.p. 203–204°C). HPLC (Macherey Nagel ET 250/8/4 NUCLEOSIL 5C18 $\lambda = 250$ nm, methanol/water (85:15): no impurity $\geq 0.1\%$). – ^{1}H NMR ($CDCl_3$/250 MHz): $\delta = 1.90$ (s, 6H, CH_3), 6.79 (d, 4H, $J = 7$ Hz, Ar*H*), 7.01 (t, 4H, $J = 7$ Hz, Ar*H*), 7.17 (t, 4H, $J = 7$ Hz, Ar*H*), 7.33 (d, 4H, $J = 7$ Hz, Ar*H*). – MS (70 eV), *m/z* (%): 358 (1), 180 (15), 179 (100), 178 (29).

Table 7. Heat capacities of the crystalline compounds **1**, **2**, **5**, and **6** determined by DSC and calculated by means of the MM3 force-field method for the gas phase

	T [K]	$Cp(c)$ [b] DSC [J mol^{-1}K^{-1}]	$Cp(g)$ [c] MM3 [J mol^{-1}K^{-1}]	ΔCp [d] [J mol^{-1}K^{-1}]
1	298	221.86	177.45	44.41
	323 [a]	241.33	192.54	48.79
2	298	255.66	200.69	54.97
	299 [a]	256.42	201.35	55.07
5	298	425.81	351.28	74.53
	343 [a]	489.41	403.72	85.69
6	298	491.97	401.69	90.28
	343 [a]	569.96	459.66	110.30

[a] T_{average}, average temperatures at which ΔH_{sub} was determined experimentally. – [b] DSC measurements. – [c] MM3 force-field calculations. – [d] $\Delta Cp = Cp(\mathrm{c}) - Cp(\mathrm{g})$.

Enthalpy of Combustion: For the measuring of the heats of combustion of **1**, **2**, **5**, and **6** an isoperibolic macrocalorimeter[36] with a stirred water bath was used. The substances were pressed into tablets of ≈300 mg weight which were burned in the calorimeter. The detailed procedure had been described previously[16]. The heat equivalent of the calorimeter was calibrated with a standard reference sample of benzoic acid (sample SRM 39i, National Bureau of Standards). The value found was $\varepsilon(J) = 25105.03 \pm 3.39$ (0.0135%) J K^{-1}. The energy for ignition was determined to be 1.46 J. The densities of the substances were determined by keeping them in suspension in solutions of NaBr of known density (Table 5). The specific heat capacities were measured by DSC (Table 5).

For the conversion of the data to standard conditions conventional procedures[37] were used. The results of the different combustion experiments are listed in Table 4.

Enthalpy of Fusion: The enthalpies of fusion of the compounds **1**, **2**, and **5** were determined by DSC. Their purities were controlled and compared with the values of GC. They were $\geq 99.99\%$ (DSC). It was not possible to determine the enthalpy of fusion of **6**, because the thermolabile dimer decomposed during melting.

Enthalpy of Sublimation: The enthalpies of sublimation $\Delta H^0_{\mathrm{sub}}$ of **1**, **2**, **5**, and **6** were determined by the method of transference in a saturated N_2 stream[15,16]. The compounds were mixed with glass beads and placed in a thermostated U tube. At several different temperatures a nitrogen stream was passed through the U tube, and the transported material was collected in a second cooled U tube. Its amount was determined by GC analysis of **1**, **2** and **5** and by HPLC analysis of **6**. Because of the low melting point of **2** we

Table 8. Heats of vaporization $\Delta H_{v,T}$ and solvent-accessible surfaces of alkyl-substituted aromatic hydrocarbons

substance	[a]	ΔH_v [kJ/mol]	surface [b] [A^2]
benzene	1	33.60 [15]	92.20
toluene	2	37.99 [15]	111.40
ethylbenzene	3	42.22 [15]	128.10
n-propylbenzene	4	46.23 [15]	145.62
cumene	5	45.10 [15]	141.60
n-butylbenzene	6	50.12 [15]	162.24
sec-butylbenzene	7	49.04 [15]	157.77
isobutylbenzene	8	48.28 [15]	157.22
tert-butylbenzene	9	48.12 [15]	153.00
ortho-xylene	10	43.43 [15]	125.82
meta-xylene	11	42.68 [15]	129.31
para-xylene	12	42.38 [15]	130.39
2-ethyltoluene	13	47.70 [15]	140.52
3-ethyltoluene	14	46.90 [15]	144.03
4-ethyltoluene	15	46.61 [15]	145.05
1,2,3-trimethylbenzene	16	49.08 [15]	140.98
1,2,4-trimethylbenzene	17	47.95 [15]	144.46
mesitylene	18	47.49 [15]	145.97
hexamethylbenzene	19	54.10 [15]	181.85
diphenylmethane	20	64.85 [44]	178.60
1,1-diphenylethane	21	66.65 [44]	191.00
1,2-diphenylethane	22	64.14 [44]	196.80
1,1-diphenylpropane	23	69.25 [44]	204.20
1,1-diphenylbutane	24	74.68 [44]	221.50
1,1-diphenyl-2-methylpropane	25	72.22 [44]	217.53
1,1-bis(4-methyl-phenyl)ethane	26	74.27 [44]	223.40
4-methylphenyl-phenylmethane	27	68.70 [44]	193.20
naphthalene	28	53.89 [15]	134.90
anthracene	29	65.27 [43]	171.07
fluorene (**1**)		65.67	166.00
9-methylfluorene (**2**)		66.44	181.90
9,9´-bifluorenyl (**5**)		95.71	283.00
9,9´-dimethyl-9,9´-bifluorenyl (**6**)		94.60	296.80
triphenylmethane	30	82.05 [42]	240.60
1,1,1-triphenylethane	31	85.56 [44]	246.17
1,1,2,2-tetraphenylethane	32	92.59 [3]	302.47
1,1,1,2-tetraphenylethane	33	101.67 [3]	300.31

[a] Index number; compare Figure 2. – [b] Calculated values; for method see experimental part.

determined the enthalpy of vaporization by the method of transference. The data are listed in Table 6.

$$\Delta H^0_{\mathrm{sub}} = R\,[\mathrm{d}\ln(m/V_{\mathrm{gas}})/\mathrm{d}T - 1] \tag{7}$$

The enthalpies of sublimation were calculated[38] from equation (7) (with R = ideal gas constant, m = amount of transported compounds, V_{gas} = volume of transportation gas, T = temperature). The values are compiled in Tables 1 and 6.

Force-Field Calculations: For calculation of the structural data the molecular models were generated with the program Chem-X[39] (molecular modelling) and their conformations optimized with the force-field program MM2[40]. The heat capacities were calculated with the force-field program MM3[41] (Table 7). The solvent-accessible surfaces were calculated with the program of Conolly[24] by using 2.5 Å as probe radius. For each molecule five surfaces were calculated with densities of 100, 105, 110, 115, and 120 points/Å^2, and we used the average of these five values. The calculated values are compiled in Table 8.

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