

Substituent Effects on the C–C Bond Strength, 15<sup>[1]</sup>  
 Geminal Substituent Effects, 7<sup>[2]</sup>

## Thermochemistry and Thermal Decomposition of Alkyl-substituted Tricyanomethyl Compounds

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The thermolysis reactions of the tricyanomethyl compounds **10a–c** were studied in solution. 2,2-Dicyano-3-methyl-3-phenylbutyronitrile (**10a**) and 2,2-dicyano-3-methyl-3-(4-nitrophenyl)butyronitrile (**10b**) decomposed heterolytically into carbenium ions and (CN)<sub>3</sub>C<sup>−</sup> anions, while 9-methyl-9-(tricyanomethyl)fluorene (**10c**) underwent about 11% homolytic C–C bond cleavage into 9-methyl-9-fluorenyl- and tricyanomethyl radicals. The rates of the homolysis were determined by a radical scavenger procedure under conditions of pseudozero order kinetics. From the temperature effect on the rate constants the activation parameters were determined [ $\Delta H^\ddagger$  (**10c**) = 155 ± 2 kJ mol<sup>−1</sup>,  $\Delta S^\ddagger$  (**10c**) = 58 ± 5 J mol<sup>−1</sup> K<sup>−1</sup>]. Standard enthalpies of formation  $\Delta H_f^\circ$  (g) were determined for 2,2-dicyanopropionitrile (**2**) (422.45 kJ mol<sup>−1</sup>), 2,2-dicyanohexanenitrile (**3**) (349.74 kJ mol<sup>−1</sup>), 2,2-dicyano-3-phenylpropionitrile (**4**) (540.75 kJ mol<sup>−1</sup>), 2-butyl-2-methylhexanenitrile (**5**) (−133.20 kJ mol<sup>−1</sup>), 2,2-dimethylpentanenitrile (**6**) (−45.78 kJ mol<sup>−1</sup>), and 2-methylbutyronitrile (**7**) (2.44 kJ mol<sup>−1</sup>) from the enthalpies of combustion and enthalpies

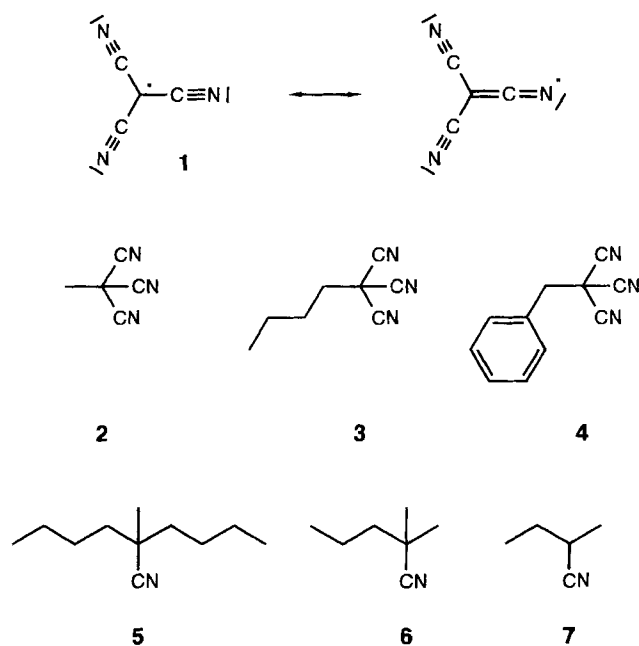
of sublimation/vaporization. From these data and known  $\Delta H_f^\circ$  (g) values for alkanenitriles and -dinitriles, thermochemical increments for  $\Delta H_f^\circ$  (g) were derived for alkyl groups with one, two, or three cyano groups attached. The comparison of these increments with those of alkanes reveals a strong geminal destabilization, which is interpreted by dipolar repulsions between the cyano groups. – From  $\Delta H_f^\circ$  (g) of **10c** and  $\Delta H^\ddagger$  of its homolytic decomposition the radical stabilization enthalpy for the tricyanomethyl radical **1**  $RSE$  (**1**) = −18 kJ mol<sup>−1</sup> was determined. Thus, **1** is destabilized, in comparison with the  $RSE$ s of tertiary  $\alpha$ -cyanalkyl (23 kJ mol<sup>−1</sup>) and  $\alpha,\alpha$ -dicyanoalkyl (27 kJ mol<sup>−1</sup>) radicals, which were recalculated from bond homolysis measurements<sup>[4]</sup> and the new thermochemical data. This change of  $RSE$  on increasing the number of  $\alpha$ -cyano groups is discussed as the result of the additive contributions by resonance stabilization and increasing destabilization by dipolar repulsion. The amount of the dipolar energies was estimated by molecular mechanics (MM2).

During the investigation of substituent effects on the homolytic dissociation of C–C bonds of substituted ethanes, we determined the stabilization energies ( $RSE$ ) of the radicals formed<sup>[3]</sup>. The  $RSE$  of monosubstituted alkyl radicals, partly of benzylic or allylic structure<sup>[3c]</sup>, were obtained from the kinetically measured enthalpies of dissociation of the *substituted* ethanes after eliminating the steric influence on the bond strength<sup>[3b]</sup>. The steric acceleration of the homolytic cleavage of peralkylated ethanes<sup>[3b]</sup> was found to be a linear function of the strain enthalpies of the ethanes. The strain enthalpies were obtained by thermochemical measurements (enthalpies of combustion) or from force-field calculations.

Recently, our interest turned from monosubstituted radicals and their precursors to those with two geminal substituents, such as  $\alpha,\alpha$ -dicyano alkyl radicals<sup>[4]</sup>, to check whether the contribution of the substituents to the  $RSE$  is additive or not. The strength of a C–C bond now, in addition, is affected by synergetic effects between the geminal substituents in the ethane or the radicals. This may be a synergetic stabilization (anomeric stabilization) as found in

acetals<sup>[3b]</sup> or the reverse effect, a synergetic destabilization, as found in malonic esters<sup>[3c]</sup> or even stronger in malononitriles<sup>[3a]</sup>.

In the present work we determined the interaction energy of three geminal cyano groups and the  $RSE$  of the tricyanomethyl radical (**1**), which were previously unknown. In addition, we revised the thermochemical increments for nitriles and geminal substituted dinitriles. We present the standard enthalpies of formation,  $\Delta H_f^\circ$  (g), obtained from the calorimetrically measured enthalpies of combustion  $\Delta H_f^\circ$  (c) and enthalpies of vaporization  $\Delta H_{vap}$ , or enthalpies of sublimation  $\Delta H_{sub}$ , respectively, for the three alkyl-substituted tricyanomethyl compounds **2–4**. So far, thermochemical data for cyano compounds had been mainly determined for *n*-alkanenitriles with carbon chains from C<sub>2</sub> up to C<sub>13</sub><sup>[5,6]</sup>. Besides for some alicyclic compounds<sup>[5,7]</sup> enthalpies of formation  $\Delta H_f^\circ$  (g) had been measured only for two branched alkanenitriles (isobutyronitrile<sup>[5]</sup> and pivalonitrile<sup>[5]</sup>). To get more precise data on secondary and tertiary nitriles for comparison and as reference compounds we have measured, in addition, the enthalpies of combus-



tion  $\Delta H_f^0(c)$  and the enthalpies of vaporization  $\Delta H_{vap}$  of the three monocyno alkanes 5–7.

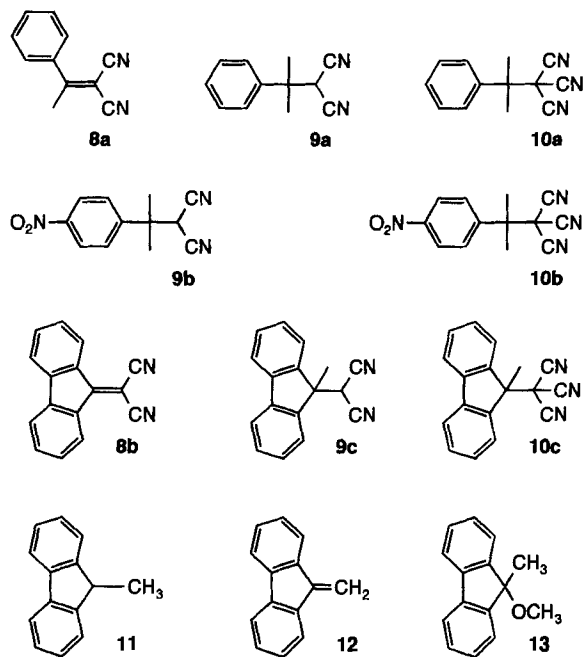
#### Formation of the Tricyanomethyl Radical 1 by Homolytic Versus Heterolytic Cleavage

The first attempt to get information about the reactivity of 1 was made by Ingold<sup>[8]</sup> who studied the decay of the tricyanomethyl radical in an EPR experiment. The radical was formed by reaction of  $\text{BrC}(\text{CN})_3$  with trichlorosilane and di-*tert*-butyl peroxide in toluene, and its EPR spectrum was detected, but no reproducible rate constants of the decay of 1 were obtained. The scatter of the experimental data was caused by a reddish-orange solid, presumably a polymer of 1; the formation of this reddish solid has also been described by other authors<sup>[8,9]</sup> and hence its precipitation seems to be characteristic of 1.

Our attempt was to generate the tricyanomethyl radical by C–C bond homolysis by using the hexasubstituted ethanes 2,2-dicyano-3-methyl-3-phenylbutyronitrile (10a<sup>[9]</sup>), 2,2-dicyano-3-methyl-3-(4-nitrophenyl)butyronitrile (10b), and 9-methyl-9-(tricyanomethyl)fluorene (10c). Compounds 10a–c were prepared by introducing a third cyano group into the malonitriles 2-cyano-3-methyl-3-phenylbutyronitrile (9a), its *p*-nitro derivative (9b) or 9-(dicyanomethyl)-9-methylfluorene (9c) using NaH and BrCN. Compounds 9a and 9c were obtained by Michael addition of methylmagnesium iodide to the corresponding  $\alpha,\beta$ -unsaturated dicyano compounds 8a<sup>[10]</sup> and 8b<sup>[11]</sup>. Compound 9b was prepared by nitration of 9a.

We started<sup>[12]</sup> with the investigation of the thermolytic cleavage of 2,2-dicyano-3-methyl-3-phenylbutyronitrile (10a)<sup>[9]</sup>. Instead of the formation of the tricyanomethyl (1) and the cumyl radicals, a heterolytic cleavage of the central  $\text{C}_q\text{--C}_q$  bond into the cumyl cation and the tricyanomethanide ion  $\text{C}(\text{CN})_3^-$  occurred. Thermolysis in benzene at 120°C in the presence of dihydroanthracene as radical scav-

enger was accelerated by addition of THF, and the major product besides a reddish, insoluble product (polymer of dicyanoketene imine)<sup>[9]</sup> was  $\alpha$ -methylstyrene, not cumene. Similar results had been obtained independently by Mitsuhashi et al.<sup>[13]</sup>.



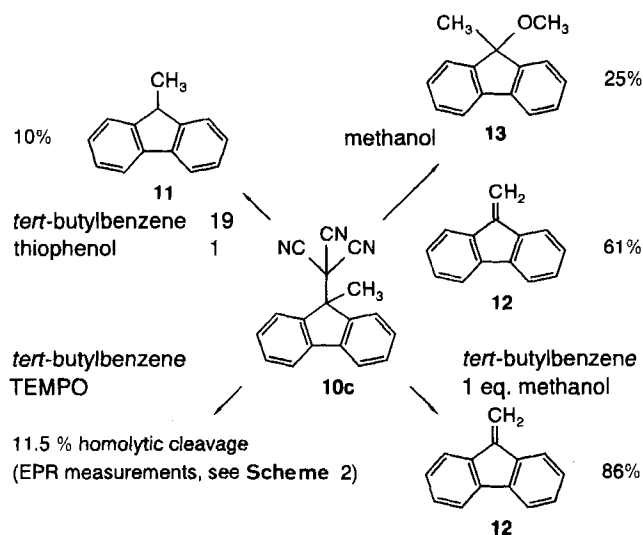
We tried to suppress the heterolytic process by introducing electron-withdrawing substituents into the alkyl group. However, the thermolysis of 2,2-dicyano-3-methyl-3-(4-nitrophenyl)butyronitrile (10b) in benzene in the presence of dihydroanthracene gave a similar product pattern as the thermolysis of 10a. The major product was  $\alpha$ -methyl-*p*-nitrostyrene, and no 2-(4-nitrophenyl)propane, the expected product of homolysis, was found. The decomposition was again accompanied by the formation of the reddish, insoluble material.

In a further experiment 9-methyl-9-(tricyanomethyl)fluorene (10c) was employed as a radical precursor. Heterolytic cleavage would result in the formation of an antiaromatic 9-methylfluorenyl cation and hence be unfavorable. The thermolysis of this compound in benzene using thiophenol as radical scavenger indicated (formation of 9-methylfluorene; detected by GC) the formation of tricyanomethyl radical 1 by homolytic C–C bond cleavage. However, the formation of an orange polymer species was still prevailing and prevented the use of different methods to determine the rate constants of the homolytic cleavage (e.g. ampoule technique<sup>[14]</sup> using mesitylene as solvent and thiophenol as radical scavenger combined with GC or HPLC analysis; UV kinetics using colored stable radicals as radical scavenger). We were forced to develop a special procedure, which was not affected by the formation of the reddish polymer and which can separate the homolytic from a possible concurrent heterolytic cleavage.

### Kinetics of the Thermolysis of 10c

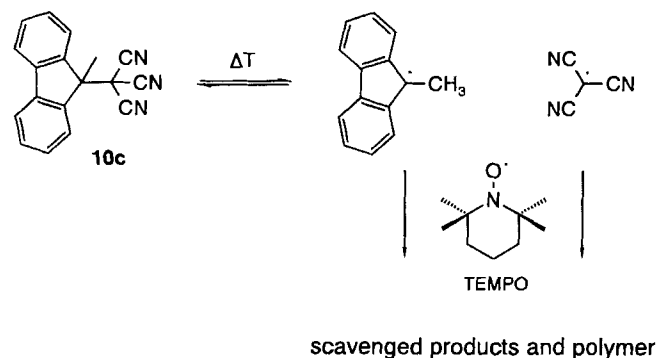
With this aim in mind the fractional yields of the products were investigated in several solvents of different polarity and reactivity (see Scheme 1). Each reaction was accompanied by the formation of reddish, insoluble polymers.

Scheme 1. Pathways for the thermolytic cleavage of dimer **10c** in solvents of different polarity using different scavengers for the 9-methylfluorenyl cation and 9-methylfluorenyl radical, respectively; products in fractional amounts



In a first attempt to probe if homolytic cleavage took place, the thermolysis of **10c** was investigated in a mixture of *tert*-butylbenzene and thiophenol (19:1) as an H donor. After 1 h at 180°C **10c** had disappeared and 9-methylfluorene (**11**) (10% yield) had been formed, presumably by homolytic cleavage of **10c** and trapping of the 9-methylfluorenyl radicals by thiophenol. The other detectable product (besides the polymer) was 9-methylenefluorene (**12**) in 20% yield. The thermolysis of **10c** in methanol (1 h; 180°C) led to **12** (61%) and to 9-methoxy-9-methylfluorene (**13**) (25%), products typically formed via a 9-methylfluorenyl cation as an intermediate. In *tert*-butylbenzene with addition of 1 equivalent of methanol (1 h; 180°C) 86% 9-methylenefluorene (**12**), but no ether **13** was obtained. Elimination via 9-methylfluorenyl cation seemed to predominate under these conditions.

Scheme 2. Thermolytic cleavage of dimer **10c** using the stable radical 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO) as radical scavenger



Apparently, the homolytic cleavage of **10c** into radicals is always accompanied by heterolytic cleavage. To measure the percentage of homolysis, we added 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO) as a radical scavenger to the solution of **10c** in *tert*-butylbenzene; TEMPO is one of the fastest trapping agents for radicals<sup>[15]</sup>. The homolysis reaction was followed by the decrease of the EPR signal intensity of TEMPO. EPR measurements between 106 and 127°C showed that the fractional amount of heterolysis and homolysis does not vary because always  $11.5 \pm 1.1\%$  homolysis occurred.

For the kinetic measurements an excess of **10c** (38 mmol l<sup>-1</sup>) over TEMPO (0.9 mmol l<sup>-1</sup>) (see Table 1) was used, which causes a decrease of the concentration of TEMPO by pseudo-zero-order kinetics.

The low concentration of the generated radicals and the steady-state situation can be expressed by the Bodenstein approximation<sup>[16]</sup>, neglecting any side reactions of the radicals (dimerization or disproportionation).

$$\frac{d[\mathbf{R}\cdot]}{dt} = 2k_1[\text{Dimer}] - k_{tr}[\mathbf{R}\cdot][\text{TEMPO}] = 0 \quad (1)$$

In eq. (1)  $[\mathbf{R}\cdot]$  stands for the sum of concentrations for both radicals formed, namely tricyanomethyl (**1**) and 9-methylfluorenyl. The change of the concentration of the radical scavenger TEMPO with time can be expressed by using eq. (2).

$$\frac{d[\text{TEMPO}]}{dt} = -k_{tr}[\mathbf{R}\cdot][\text{TEMPO}] \quad (2)$$

Combining eqs. (1) and (2) yields equation (3), which can be used to determine the rate constants  $k_1$  from the measured decrease of TEMPO,  $d[\text{TEMPO}]/dt$  (see Figure 1), and the average concentration of **10c** [Dimer].

$$\frac{d[\text{TEMPO}]}{dt} = -2k_1[\text{Dimer}] \quad (3)$$

The latter results from the initial concentration of the stock solution (see Experimental), diminished by the fractional amount of decomposition by homolysis and heterolysis, and the volume expansion during heating up.

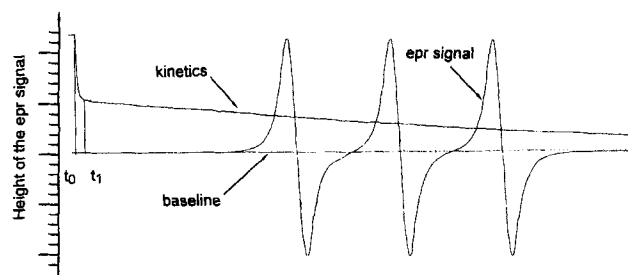


Figure 1. EPR kinetics of dimer **10c** (see Scheme 2). The EPR signal was the overmodulated (1G) signal of TEMPO at room temperature. The kinetics of the thermolytic cleavage of **10c** was followed by the signal height of the central peak of the TEMPO EPR signal. The kinetic measurement started at  $t_0$  (room temp.), and the signal height was followed after heating ( $t_1$ ) the probe up to the temperatures indicated in Table 1

The rate constants were measured at different temperatures (Table 1). Using the standard deviations of the  $k_1$  values as weighting factors<sup>[17]</sup>, we calculated the Eyring activation parameters for the homolysis of **10c** given in Table 1.

The enthalpies of sublimation/vaporization of compounds **2–7** were determined from their equilibrium vapor pressures, measured by the amount of gaseous material being transported<sup>[24]</sup> in a nitrogen stream which was saturated

Table 1. Rate constants and activation parameters for the homolytic cleavage of 9-methyl-9-tricyanomethylfluorene (**10c**) in *tert*-butylbenzene in the presence of 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO) as radical scavenger

T [a] [K]	d[TEMPO]/dt [b] [ $\mu\text{mol l}^{-1}\text{s}^{-1}$ ]	$c_T(t_1)$ [c] [mmol l <sup>-1</sup> ]	$c_D(t_1)$ [d] [mmol l <sup>-1</sup> ]	conversion[e] [%]	$c_{\text{Dimer}}(t_{\text{av}})$ [f] [mmol l <sup>-1</sup> ]	k [g] [10 <sup>-6</sup> s <sup>-1</sup> ]	$\sigma$ [%] [h]
365.65	0.0280	0.889	32.35	11.9	30.43	0.460	0.19
376.15	0.136	0.889	32.35	11.9	30.43	2.24	0.50
386.75	0.531	2.427	34.78	30.3	29.51	9.00	2.0
386.75	0.559	2.427	34.78	30.3	29.51	9.47	2.1
386.75	0.545	2.427	34.78	30.3	29.51	9.23	2.1
397.35	1.95	2.427	34.09	31.0	28.81	33.8	7.6
397.35	2.08	2.427	34.09	31.0	28.81	36.1	8.0
397.35	1.75	2.427	34.09	31.0	28.81	30.4	6.5
397.35	1.74	2.427	34.09	31.0	28.81	30.2	6.8
402.25	3.22	2.427	33.39	31.6	28.11	57.3	2.5
402.25	3.43	2.427	33.39	31.6	28.11	61.0	2.6
402.25	3.37	2.427	33.39	31.6	28.11	59.9	2.6
	$\Delta G^\ddagger(300)$ [kJ mol <sup>-1</sup> ]	$\Delta H^\ddagger$ [kJ mol <sup>-1</sup> ]		$\Delta S^\ddagger$ [J mol <sup>-1</sup> K <sup>-1</sup> ]		$T_{1/2}$ [K] [i]	
<b>10c</b>	122.0 ± 2.2	155.4 ± 2.2		58.3 ± 5.5		412.5	

[a] Temperature in the EPR cavity. – [b] Decrease of the radical scavenger TEMPO determined by use of the linear correlation between signal height and reaction time. – [c] Concentration of the TEMPO stock solution at  $t_1$ . – [d] Concentration of dimer **10c** at the time  $t_1$ ; calculated from the concentration of the stock solution and the volume expansion coefficient,  $\alpha_T = 9.60 \cdot 10^{-4}$  of *n*-butylbenzene<sup>[38]</sup> and the fractional decomposition during heating up. – [e] Conversion of **10c** by homolytic and heterolytic cleavage at the end of the kinetic run. – [f] Average concentration of **10c** during the kinetic run. – [g] Rate constants  $k$  for the homolysis of dimer **10c** according to eq. (3). – [h] Standard deviation in the rate constants  $k$ . – [i] Temperature at which half life is 1 h.

## Thermochemistry

**Synthesis:** The alkyl-substituted tricyanomethyl compounds 2,2-dicyanopropionitrile (**2**), 2,2-dicyanohexanenitrile (**3**), and 2,2-dicyano-3-phenylpropionitrile (**4**) were prepared<sup>[18]</sup> in refluxing acetonitrile by alkylating potassium tricyanomethanide<sup>[19]</sup> with iodomethane, iodobutane, or benzyl bromide, respectively. Purification was achieved by repeated sublimation of **2** and **4** and by distillation of **3** with a spinning band column. In the samples no impurities ( $\geq 0.001\%$ ) could be detected by GC. DSC measurements of the melting process<sup>[20]</sup> support a purity of  $\geq 99.99\%$  for **2** and **4**.

The enthalpies of combustion  $\Delta H_c(c)$  of **2–7** were measured in an aneroid isoperibolic macrocalorimeter<sup>[21]</sup>, and standard enthalpies of formation for the crystalline phase  $\Delta H_f^0(c)$  were derived (Table 2). Details are given in the experimental section. From an earlier investigation of the combustion of 2,2-dicyanopropionitrile (**2**) of lower purity ( $\approx 99\%$ )<sup>[22]</sup>  $\Delta H_f^0(2, c) = 353.1 \pm 5.0$  kJ mol<sup>-1</sup> had been reported<sup>[18]</sup>. This value resulted from only two combustion experiments. Our new result for  $\Delta H_f^0(2, c) = 348.6 \pm 2.03$  kJ mol<sup>-1</sup> (Table 2) increases the precision of this value. The enthalpies of formation  $\Delta H_f^0(c)$  of **3** ( $288.7 \pm 2.0$  kJ mol<sup>-1</sup>) and **4** ( $444.5 \pm 1.17$  kJ mol<sup>-1</sup>) were determined for the first time.

over the finely powdered substance 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<sup>[25]</sup>. From the linear correlation between  $\ln p'$  and  $1/T$ , the enthalpy of sublimation  $\Delta H_{\text{sub},T}^0$  at the temperature  $T$  was obtained. The sublimation enthalpies  $\Delta H_{\text{sub},T}^0$  are recorded in Table 2.

The resulting standard enthalpies of formation for the gas phase  $\Delta H_f^0(g)$  are given in Table 2. With the new  $\Delta H_f^0(g)$  values for **5–7** we repeated the calculation of increments for the enthalpies of formation by multiple linear regression. In a change from our previous work<sup>[7]</sup> we used a more reliable value for the enthalpy of formation  $\Delta H_f^0(g)$  of acetonitrile of  $74.06 \pm 0.38$  kJ mol<sup>-1</sup><sup>[26]</sup>, which was determined by two independent laboratories.

This leads to a change of the value for the CN ([CN] = 116.11 kJ mol<sup>-1</sup>) increment, because we base our definition of group increments on a common value for all methyl groups ( $\text{CH}_3[\text{CN}] \equiv \text{CH}_3[\text{C}]$ ). Thus, consequently the improved values for other increments differ from our former results<sup>[3a]</sup> (see Table 4). The  $\Delta H_f^0(g, \text{RCN})$  values used for the calculation of the increments are listed in Table 3. The mean deviations between the experimental enthalpies of formation  $\Delta H_f^0(g, \text{RCN})$  and the values calculated from the

Table 2. Thermodynamic data for 2,2-dicyanopropionitrile (2), 2,2-dicyanohexanenitrile (3), 2,2-dicyano-3-phenylpropionitrile (4), 2-*n*-butyl-2-methylhexanenitrile (5), 2,2-dimethylpentanenitrile (6), and 2-methylbutyronitrile (7) for the condensed phase and for the gas phase [kJ mol<sup>-1</sup>]<sup>[a]</sup>

	$\Delta H_c^\circ$ (c)	$\Delta H_f^\circ$ (c)	$\Delta H_{fus,T}^{[b]}$	$\Delta H_{vap,T}$	$\Delta H_{sub,T}^\circ$	$\Delta H_f^\circ$ (g)
2	-2744.86 (± 1.01)	348.57 (± 1.02)	18.70 (± 0.21)	55.18 [c]	73.88 (± 0.46)	422.45 (± 1.12)
3	-4723.05 (± 1.53)	288.74 (± 1.55)	-	61.00 (± 0.21)	-	349.74 (± 1.56)
4	-5773.52 (± 0.58)	444.52 (± 0.63)	29.29 (± 0.21)	66.94 [c]	96.23 (± 0.38)	540.75 (± 0.74)
5	-7136.83 (± 1.36)	-192.99 (± 1.42)	-	59.79 (± 0.38)	-	-133.20 (± 1.47)
6	-4519.78 (± 0.69)	-92.68 (± 0.75)	-	46.90 (± 0.42)	-	-45.78 (± 0.86)
7	-3213.75 (± 1.39)	-40.03 (± 1.41)	-	42.47 (± 0.29)	-	2.44 (± 1.44)

[a] Standard deviations in brackets. – [b] DSC measurements. – [c]  $\Delta H_{vap,T} = \Delta H_{sub,T}^\circ - \Delta H_{fus,T}$ .

Table 3. Values  $\Delta H_f^\circ$  (g) [kJ mol<sup>-1</sup>] for aliphatic and aromatic nitriles used for the determination of the increments  $\text{CH}_2[\text{CN},\text{C}]$ ,  $\text{CH}[\text{CN},\text{C}_2]$ , and  $\text{C}[\text{CN},\text{C}_3]$  (see Table 4)

Substance	$\Delta H_f^\circ$ (g)	$\Delta$ <sup>[a]</sup>
Acetonitrile	74.06 ± 0.38	0.0
Propionitrile	51.50 ± 0.59	4.2
Butyronitrile	33.76 ± 1.09	0.5
Isobutyronitrile	23.30 ± 1.30	1.0
2-Methylbutyronitrile (7)	2.43 ± 1.42	0.5
Pivalonitrile	-2.51 ± 0.79	-0.7
Pentanitrile	10.42 ± 1.46	2.3
Cyclohexanenitrile	4.77 ± 0.67	-1.5
Heptanenitrile	-30.96 ± 1.30	0.8
Octanenitrile	-50.46 ± 1.51	-1.2
Decanenitrile	-91.50 ± 1.80	3.1
Dodecanenitrile	-113.51 ± 2.01	-2.5
Tetradecanenitrile	-174.89 ± 2.72	-5.5
2,2-Dimethylpentanenitrile (6)	-45.77 ± 0.88	-0.3
2-Butyl-2-methylhexanenitrile (5)	-133.22 ± 1.51	1.3
Benzonitrile	215.69 ± 2.13	0.6

[a] Difference between  $\Delta H_f^\circ$  (g) and the sum of the group increments.

group increments (Table 4) are small (± 2.22 kJ mol<sup>-1</sup>). The larger deviations for two compounds [propionitrile  $\Delta = 4.2$  kJ mol<sup>-1</sup> and tetradecanenitrile  $\Delta = -5.5$  kJ mol<sup>-1</sup> (Table 3)] might be due to systematic errors in the experimental data. The increments  $\text{CH}_2[\text{CN},\text{C}]$ ,  $\text{CH}[\text{CN},\text{C}_2]$ , and  $\text{C}[\text{CN},\text{C}_3]$  are based on measurements on 8, 4, or 3 compounds respectively.

Table 4. Improved increments in enthalpy of formation [kJ mol<sup>-1</sup>] for alkyl ( $\Delta H_{\text{alkyl}}$ ), nitrile ( $\Delta H_{\text{nitrile}}$ ), dinitrile ( $\Delta H_{\text{dinitrile}}$ ), trinitrile ( $\Delta H_{\text{trinitrile}}$ ), and tetranitrile ( $\Delta H_{\text{tetranitrile}}$ )<sup>[a]</sup>

$\Delta H_{\text{alkyl}}$	$\Delta H_{\text{nitrile}}$	$\Delta H_{\text{dinitrile}}$	$\Delta H_{\text{trinitrile}}$	$\Delta H_{\text{tetranitrile}}$
$\text{CH}_3[\text{C}]$ -42.05	$\text{CH}_3[\text{CN}]$ -42.05	-- --	-- --	-- --
$\text{CH}_2[\text{C}_2]$ -21.48	$\text{CH}_2[\text{CN},\text{C}]$ -18.37	$\text{CH}_2[(\text{CN})_2]$ 33.9	-- --	-- --
$\text{CH}[\text{C}_3]$ -9.04	$\text{CH}[\text{CN},\text{C}_2]$ -7.66	$\text{CH}[(\text{CN})_2,\text{C}]$ 26.8	$\text{CH}[(\text{CN})_3]$ (131.9) <sup>[b]</sup>	-- --
$\text{C}[\text{C}_4]$ -1.26	$\text{C}[\text{CN},\text{C}_3]$ 6.86	$\text{C}[(\text{CN})_2,\text{C}_2]$ 40.2	$\text{C}[(\text{CN})_3,\text{C}]$ 115.5	$\text{C}[(\text{CN})_4]$ 208.4

[a] Neighboring atoms in square brackets (values for comparison<sup>[7]</sup> see footnote<sup>[c]</sup>). – [b] The substance  $\text{HC}(\text{CN})_3$  can not be isolated; it is available only as an aqueous solution<sup>[9]</sup>. Therefore the value for this group increment was calculated from the enthalpy of formation obtained from ab initio calculations<sup>[39]</sup>. – [c]  $\text{CH}_3[\text{CN}] = -42.05$ ,  $\text{CH}_2[\text{CN},\text{C}] = -8.08$ ,  $\text{CH}[\text{CN},\text{C}_2] = 1.05$ ,  $\text{C}[\text{CN},\text{C}_3] = 12.59$ ,  $\text{CH}_2[(\text{CN})_2] = 53.2$ ,  $\text{CH}[(\text{CN})_2,\text{C}] = 46.2$ , and  $\text{C}[(\text{CN})_2,\text{C}_2] = 50.5$  kJ mol<sup>-1</sup>.

The increments for malononitrile and the alkylsubstituted malononitriles  $\text{CH}_2[(\text{CN})_2]$ ,  $\text{CH}[(\text{CN})_2,\text{C}]$ , and  $\text{C}[(\text{CN})_2,\text{C}_2]$ <sup>[7]</sup> were recalculated with the new CN group increments obtained above. The increment  $\text{C}[(\text{CN})_3,\text{C}]$  for alkyl-substituted tricyano compounds was calculated from  $\Delta H_f^\circ$  (g) values of the compounds 2, 3, and 4 and is compiled in Table 4. The differences between the enthalpies of formation and the calculated ones from the group increments are 0.6 (2), -7.6 (3), and 6.2 (4) kJ mol<sup>-1</sup>.

## Results and Discussion

The new group increments for cyano compounds  $\text{CH}_x[\text{CN},\text{C}_{3-x}]$  show that the introduction of a cyano group instead of an alkyl group causes a destabilization of 3.1, 1.4, and 8.0 kJ mol<sup>-1</sup> ( $x = 2, 1, 0$ ), respectively (see Table 5). The absolute values of the new increments for malononitriles differ from the former values<sup>[7]</sup>, however the size of the synergetic effect in these groups remains unchanged. The synergetic effect is given by the difference of the experimental result and the hypothetical energy calculated by assuming additivity. The latter is the sum of the alkyl group increment ( $H_{\text{alkyl}}$ ) and twice or thrice the difference of energy caused by mono substitution by one CN group ( $\Delta H_{\text{nitrile}} - \Delta H_{\text{alkyl}}$ ; see Table 5 and footnotes). It turns out that the geminal interaction between CN groups destabilizes polynitriles. The synergetic destabilization increases with the number of CN groups up to 177.2 kJ mol<sup>-1</sup> in  $\text{C}(\text{CN})_4$  (Table 5). The size of the geminal destabilization decreases with the number of alkyl groups. Thus, malononitrile itself is destabilized by 49.2 kJ mol<sup>-1</sup> and  $\alpha,\alpha$ -dialkylmalononitriles by only 25.2 kJ mol<sup>-1</sup> (Table 5). Alkyl-substituted tricyanomethyl compounds (i.e. 2–4) are destabilized by 92.4 kJ mol<sup>-1</sup>.

These observed geminal destabilizations (see Table 5) arise mainly from repulsive forces between the CN groups by dipolar interactions. These forces can be modelled by force-field calculations. From MM2 calculations (see Experimental; Table 10) one obtains a dipolar contribution to the steric energy of 27.9 and 83.1 kJ mol<sup>-1</sup> for the  $\text{C}[(\text{CN})_2,\text{C}_2]$  and  $\text{C}[(\text{CN})_3,\text{C}]$  moieties, respectively. These calculated values accord remarkably well with the measured geminal destabilizations;  $\Delta\Delta H_{\text{gem. C}[(\text{CN})_2,\text{C}_2]} = 25.2$  and  $\Delta\Delta H_{\text{gem. C}[(\text{CN})_3,\text{C}]} = 92.4$  kJ mol<sup>-1</sup> (see Table 5).

To deduce the *RSE* of the tricyanomethyl radical (1) from the C–C bond dissociation energy of 10c the steric effect

Table 5. Geminal destabilization  $\Delta\Delta H_{\text{gem}}$  [kJ mol<sup>-1</sup>] of aliphatic malononitriles, alkyl-substituted tricyano compounds, and for tetracyanomethane obtained from the newly determined increments (Table 4) for calculation

	$\Delta H_{\text{nitrite}} - \Delta H_{\text{alkyl}}$ [a]	$\Delta\Delta H_{\text{gem. dinitrile}}$ [b]	$\Delta\Delta H_{\text{gem. trinitrile}}$ [c]	$\Delta\Delta H_{\text{gem. tetranitrile}}$ [d]
CH <sub>2</sub> [(CN) <sub>x</sub> , C <sub>2-x</sub> ]	3.1	49.2	-	-
CH[(CN) <sub>x</sub> , C <sub>3-x</sub> ]	1.4	33.1	136.8[e]	-
C[(CN) <sub>x</sub> , C <sub>4-x</sub> ]	8.1	25.2	92.4	177.2

[a] Values determined with the calculated values of Table 4. - [b]  $\Delta\Delta H_{\text{gem. dinitrile}} = \Delta H_{\text{dinitrile}}$  (Table 4) - 2( $\Delta H_{\text{nitrite}} - \Delta H_{\text{alkyl}}$ ) (column 1) -  $\Delta H_{\text{alkyl}}$ . - [c]  $\Delta\Delta H_{\text{gem. trinitrile}} = \Delta H_{\text{trinitrile}}$  (Table 4) - 3( $\Delta H_{\text{nitrite}} - \Delta H_{\text{alkyl}}$ ) (column 1) -  $\Delta H_{\text{alkyl}}$ . - [d]  $\Delta\Delta H_{\text{gem. tetranitrile}} = \Delta H_{\text{tetranitrile}}$  (Table 4) - 4( $\Delta H_{\text{nitrite}} - \Delta H_{\text{alkyl}}$ ) (column 1) -  $\Delta H_{\text{alkyl}}$ . - [e] Based on ab initio calculations only<sup>[39]</sup>, Table 4, footnote<sup>[b]</sup>.

for the dissociation process had to be determined. During the homolytic dissociation of a dimer into radicals a release of strain enthalpy  $D_s$  occurs, which is caused by the difference of the strain enthalpy  $H_s$  in the dimer and the strain enthalpies  $H_s$  in the radicals. As an estimate of this strain of dissociation,  $D_s = H_s(R_1 - R_2) - H_s(R_1 \cdot) - H_s(R_2 \cdot)$ , we used the strain difference between the dimer and the monomers  $RH$ ,  $D_s' = H_s(R_1 - R_2) - H_s(R_1H) - H_s(R_2H)$ <sup>[3b]</sup>. The value  $D_s'$  (**10c**) was calculated to be 11.63 kJ mol<sup>-1</sup> by using the MM2 force-field method. This value corresponds to a small steric acceleration. The steric acceleration of the thermolysis of a series of hexaalkylethanes had been measured previously<sup>[27]</sup> and expressed in the linear correlation between  $\Delta G^\ddagger$  (300°C) and  $D_s$ .

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

From this correlation one can calculate the value of  $\Delta G_{300}^\ddagger$  for a reference alkane with a similar  $D_s'$  value as **10c**,  $\Delta G_{300}^\ddagger(\text{hexaalkylethanes}, D_s' = 11.63 \text{ kJ mol}^{-1}) = 254.7 (\pm 3.7) \text{ kJ mol}^{-1}$ . The difference between this reference value for an unsubstituted alkane and the experimental  $\Delta G_{300}^\ddagger$  (**10c**) corresponds to the substituent effect in **10c** on its rate of dissociation (eq. 5), independent of steric effects.

$$\Delta\Delta G_{300}^\ddagger = \Delta G^\ddagger(\text{hexaalkylethanes}, D_s' = 11.63 \text{ kJ mol}^{-1}) - \Delta G_{300}^\ddagger(\text{10c}) \quad (5)$$

$$= 254.7 (\pm 3.7) - 122.0 (\pm 2.2) = 132.7 (\pm 4.30) \text{ kJ mol}^{-1}$$

$\Delta\Delta G_{300}^\ddagger$  can be converted to a  $\Delta\Delta H^\ddagger$  value by using the experimentally determined value for  $\Delta S^\ddagger$  (**10c**) = 58.3 ( $\pm 5.5$ ) J mol<sup>-1</sup> K<sup>-1</sup> and the mean value of the reference system  $\bar{\Delta S}^\ddagger$  (**10c**) (hexaalkylethanes) = 67.8 ( $\pm 7.1$ ) J mol<sup>-1</sup> K<sup>-1</sup><sup>[3b]</sup> (eq. 6).

$$\Delta\Delta H^\ddagger = \Delta\Delta G_{300}^\ddagger + 0.573 [\Delta S^\ddagger(\text{hexaalkylethanes}) - \Delta S^\ddagger(\text{10c})] \quad (6)$$

$$= 132.7 (\pm 4.30) + [0.573 (67.8 - 58.3)] = 138.1 (\pm 4.3) \text{ kJ mol}^{-1}$$

This enthalpy value  $\Delta\Delta H^\ddagger = 138.1 (\pm 4.3) \text{ kJ mol}^{-1}$  is the sum of the radical stabilization energies of the radicals formed, namely the tricyanomethyl radical (**1**) and the 9-methylfluorenyl radical, and the synergetic geminal effect in the ground state.

The latter can be deduced from the group increments of Table 4. The difference between a group bearing three cy-

ano substituents and another bearing three alkyl groups (Table 5) leads to a synergetic effect  $\Delta\Delta H_{\text{gem}}$  of 92.4 ( $\pm 4.2$ ) kJ mol<sup>-1</sup>.

The radical stabilization energy  $RSE$  for the tricyanomethyl radical (**1**) was then calculated by using the radical stabilization energy for the 9-methylfluorenyl radical itself;  $RSE$  (9-methylfluorenyl) = 64 ( $\pm 8$ ) kJ mol<sup>-1</sup><sup>[3c]</sup>.

$$RSE(\text{1}) = \Delta\Delta H^\ddagger - RSE(9\text{-methylfluorenyl}) - \Delta\Delta H_{\text{gem. (trinitrile)}} \\ = 138.1 (\pm 4.3) - 64.0 (\pm 8.0) - 92.4 (\pm 4.2) \\ = -18.3 (\pm 10.0) \text{ kJ mol}^{-1} \quad (7)$$

The radical stabilization energy  $RSE$  for a tertiary dicyanoalkyl radical was also recalculated according to the procedure given for the tricyanomethyl radical (**1**).

$$RSE[\bullet C(C, (CN)_2)] = \Delta\Delta H^\ddagger - \Delta\Delta H_{\text{gem. (dinitrile)}} \\ = 51.9 (\pm 3.8) - 25.2 (\pm 5.4) = 26.7 (\pm 6.6) \text{ kJ mol}^{-1}$$

The value for the radical stabilization energy  $RSE$  of a tertiary cyanodialkyl radical was determined in previous work to be  $RSE[\bullet C(C_2, CN)] = 23.0 \text{ kJ mol}^{-1}$ <sup>[28]</sup>.

Thus, a  $RSE = 23.0 \text{ kJ mol}^{-1}$  is obtained for  $\bullet C(C_2, CN)$  and  $RSE = 26.7 \text{ kJ mol}^{-1}$  for  $\bullet C[C, (CN)_2]$ , and a destabilization of  $-18.3 \text{ kJ mol}^{-1}$  is found for  $\bullet C(CN)_3$ . According to additivity, resonance stabilization should increase by roughly the same amount going from  $\bullet C(C_2, CN)$  to  $\bullet C[C, (CN)_2]$  and  $\bullet C(CN)_3$ . However, dipolar destabilization, which was measured for the alkyl groups  $C[(CN)_2, C_2]$  and  $C[(CN)_3, C]$  (see Table 5) in the ground state caused by dipolar repulsion of the geminal CN groups, must be also present in the radicals. To obtain information about the dipolar repulsions in the radicals, MM2 calculations were performed for the planar<sup>[8]</sup> dicyano- and tricyanoalkyl radicals. The parameters (see Experimental) were adapted to fit the MM2 parameters for radicals<sup>[29]</sup>. Dipolar repulsion energies of 16.3 and 69.7 kJ mol<sup>-1</sup> were calculated by this method for  $\bullet C[C, (CN)_2]$  and  $\bullet C(CN)_3$  respectively. These data explain the observed  $RSE$ . The amount of  $\approx 16 \text{ kJ mol}^{-1}$  dipolar interaction reduces the inherent resonance stabilization by two CN groups [roughly two times  $RSE$   $\bullet C(CN, C_2) = 23 \text{ kJ mol}^{-1}$ ] to an estimated  $RSE$   $[\bullet C(C, (CN)_2)] \approx 30 \text{ kJ mol}^{-1}$ , which corresponds to the observed  $RSE$   $[\bullet C(C, (CN)_2)] = 26.7 \text{ kJ mol}^{-1}$ . The strong decrease of the  $RSE$  of  $\bullet C(CN)_3$  compared to the expected increase (compared to the dicyano or monocyno radicals) can be explained also by the strong dipolar repulsion ( $\approx 70 \text{ kJ mol}^{-1}$  in **1**). This dipolar repulsion causes a negative radical stabilization energy  $RSE$  (**1**) for the tricyanomethyl radical (**1**).

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## Experimental

All compounds were handled under N<sub>2</sub> by using carefully dried glassware and carefully dried solvents. - <sup>1</sup>H NMR: Bruker WM 250 (250 MHz); Bruker AM 400 (400 MHz); <sup>13</sup>C NMR: Bruker

Table 6. Results of typical experiments of combustion calorimetry of 2,2-dicyanopropionitrile (2), 2,2-dicyanohexanenitrile (3), 2,2-dicyano-3-phenylpropionitrile (4), 2-butyl-2-methylhexanenitrile (5), 2,2-dimethylpentanenitrile (6), and 2-methylbutyronitrile (7)

x	2(1)	2(5)	3(7)	4(2) <sup>[f]</sup>	5(4)	6(3)	7(5)
$m(x)[g]$ <sup>[a]</sup>	0.353098	0.377468	0.333712	0.348050	0.283331	0.278974	0.291612
$m_{\text{polyethylene}}$ <sup>[a]</sup>	-	0.035738	0.527556	0.043024	0.503669	0.494650	0.571434
$m_{\text{cotton}}$ <sup>[a]</sup>	0.000784	0.000820	0.000952	0.001069	0.001044	0.000930	0.000949
$\Delta T_c [K]$ <sup>[b]</sup>	0.36956	0.42763	1.40375	0.52259	1.41325	1.36723	1.50661
$\epsilon_{\text{calor}}(-\Delta T_c)[J]$ <sup>[c]</sup>	-9274.46	-10731.94	-35228.68	-13119.64	-35455.73	-34301.27	-37797.92
$\epsilon_{\text{cont}}(-\Delta T_c)[J]$ <sup>[c]</sup>	-4.86	-5.62	-20.35	-7.07	-20.36	-19.63	-22.43
$\Delta E_{\text{dec}}(\text{HNO}_x)[J]$ <sup>[d]</sup>	36.60	40.42	47.76	-	20.99	30.44	13.86
$\Delta E_{\text{corr}}[J]$ <sup>[d]</sup>	7.05	8.28	14.67	7.99	12.15	12.02	13.86
$-m_{\text{polyethyl.}} \Delta u_c [J]$ <sup>[d]</sup>	-	816.83	24464.31	1978.53	23356.60	22938.34	26499.07
$-m_{\text{cotton}} \Delta u_c [J]$ <sup>[d]</sup>	13.28	13.89	16.13	18.12	17.69	15.75	16.07
$\Delta u_c(x)[J g^{-1}]$	-26114.3	-26112.6	-32077.6	-31859.8	-42590.5	-40587.6	-38595.8
$\Delta H_c(x)[kJ mol^{-1}]$ <sup>[e]</sup>	-2742.75	-2742.57	-4723.08	-5773.2	-7137.02	-4519.69	-3212.97
$\Delta H_f(x)[kJ mol^{-1}]$ <sup>[e]</sup>	346.46	346.28	288.77	444.2	-192.79	-92.77	-40.81

<sup>[a]</sup>  $m$ : air-reduced masses. – <sup>[b]</sup>  $\Delta T_c = T_f - T_i + \Delta T_{\text{corr}}$ ;  $T_h = 298.15 \text{ K}$ ;  $V_{\text{bomb}} = 0.2664 \text{ l}$ ;  $p_{\text{gas}}^i = 30.00 \text{ atm}$  (30.40 bar);  $m_{\text{water}}^i = 0.78 \text{ g}$ ;  $E_{\text{ignit}} = 1.46 \text{ J}$ ;  $T_i = 297.5 \text{ K}$ ;  $m_{\text{platinup}} = 9.763 \text{ g}$ . – <sup>[c]</sup>  $\epsilon_{\text{calor}}$  from calibration measurements with benzoic acid;  $\epsilon_{\text{cont}}(-\Delta T_c) = \epsilon_{\text{cont}}(T_i - 298 \text{ K}) + \epsilon_{\text{cont}}(298 \text{ K} - T^r + \Delta T_{\text{corr}})$ . – <sup>[d]</sup>  $\Delta E_{\text{corr}}$ : sum of the items 81–85, 87–90, 93, and 94 reported in ref.<sup>[33]</sup>;  $-m_{\text{cotton}} \Delta u_c$ ,  $-m_{\text{polyethylene}} \Delta u_c$ , and  $-m_{\text{oil}} \Delta u_c$ : amounts of heat released by the combustion of the auxiliary compounds.  $\Delta E_{\text{dec}}(\text{HNO}_x)$ : amount of enthalpy change by the formation of  $\text{HNO}_3/\text{HNO}_2$ , determined by titration<sup>[35]</sup>. – <sup>[e]</sup> Average from several measurements, see Table 2. – <sup>[f]</sup> Using oil instead of polyethylene as auxiliary compound.

Table 7. Standard heats of formation  $\Delta H_f(x)$  [ $\text{kJ mol}^{-1}$ ] (liquid or solid state) as result of all combustion experiments

	2	3	4	5	6	7
1	346.46	295.18	444.2	-197.38	-94.57	-44.85
2	351.74	286.37	444.2	-194.00	-90.47	-39.22
3	349.27	285.12	446.8	-189.20	-92.77	-38.78
4	349.10	297.00	443.9	-192.79	-93.47	-36.48
5	346.28	283.89	443.5	-191.57	-92.13	-40.81
6	-	284.88	-	-	-	-
7	-	288.77	-	-	-	-
8	-	289.50	-	-	-	-
9	-	287.95	-	-	-	-
<sup>[a]</sup>	348.57 ( $\pm 1.02$ )	288.74 ( $\pm 1.55$ )	444.52 ( $\pm 0.63$ )	-192.99 ( $\pm 1.42$ )	-92.68 ( $\pm 0.75$ )	-40.03 ( $\pm 1.41$ )

<sup>[a]</sup> Mean value and standard deviation.

AM 400 (100 MHz); solvent  $\text{CDCl}_3$ , TMS as internal standard. – GC: Carlo Erba Fraktometer Vega Series GC 6000, Hewlett Packard Integrator 3390A,  $\text{N}_2$  flow 2 ml/min, SE-30 capillary columns 25 m. Standard temperature program:  $100^\circ\text{C}$  for 5 min; with  $10^\circ\text{C}/\text{min}$  up to  $250^\circ\text{C}$ . – MS: Varian Fraktometer 3700, Finnigan Mat 44s. – HPLC: Waters pump 6000A, Merck-Hitachi UV-Vis detector, Machery-Nagel column ET 250/8/4 NUCLEOSIL 5C18. – Melting points: Büchi apparatus (Dr. Tottoli), the melting points are uncorrected. – DSC: Perkin-Elmer DSC-2C with Olivetti PC M 28. – EPR: Bruker BER-420; field controller B-H15; microwave unit ER 048R.

2,2-Dicyanopropionitrile (2) was prepared as described in the literature<sup>[18,22]</sup> by refluxing 32.77 g (254 mmol) of potassium tricyanmethanide and 51.25 g (361 mmol) of methyl iodide in 200 ml of acetonitrile for 72 h. After removal of the solvent the raw product was diluted with water and extracted several times with diethyl ether. The combined organic layers were dried with  $\text{Na}_2\text{SO}_4$ . Purification was performed by recrystallization from  $\text{CH}_2\text{Cl}_2$  and repeated sublimation to remove any traces of solvents; yield of 2 8.3

g (31%), mp  $94^\circ\text{C}$  (ref.<sup>[18]</sup> 53%, mp  $94\text{--}95^\circ\text{C}$ ), GC: no impurity  $\geq 0.001\%$ . –  $^1\text{H NMR}$  ( $\text{CDCl}_3/400 \text{ MHz/TMS}$ ):  $\delta = 2.30$  (s,  $\text{CH}_3$ ). –  $^{13}\text{C NMR}$  ( $\text{CDCl}_3/400 \text{ MHz/TMS}$ ):  $\delta = 23.3$  [ $\text{C}(\text{CN})_3$ ], 25.6 ( $\text{CH}_3$ ), 108.4 (CN). – IR (KBr):  $\tilde{\nu} = 3000 \text{ cm}^{-1}$ , 2240, 1450, 1435. – MS (70 eV),  $m/z$  (%): 105 (3), 104 (10), 79 (28), 78 (100), 77 (52), 76 (25), 64 (39).

2,2-Dicyanohexanenitrile (3) was synthesized according to the procedure used for the preparation of 2. A brown oil was obtained, which was distilled in a spinning band column. Yield of 3 26%; bp  $120^\circ\text{C}/0.3 \text{ mbar}$ . GC: no impurity  $\geq 0.001\%$ . –  $^1\text{H NMR}$  ( $\text{CDCl}_3/250 \text{ MHz/TMS}$ ):  $\delta = 1.02$  (t, 3H,  $J = 8 \text{ Hz}$ ,  $\text{CH}_3$ ), 1.53 (sext, 2H,  $J = 8 \text{ Hz}$ ,  $\text{CH}_3\text{CH}_2$ ), 1.76 (m, 3H,  $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 2.44 [m, 2H,  $\text{CH}_2\text{C}(\text{CN})$ ]. – IR (film):  $\tilde{\nu} = 2940 \text{ cm}^{-1}$ , 2910, 2850, 2240. – MS (70 eV),  $m/z$  (%): 146 (2), 132 (9), 91 (59), 79 (58), 57 (51), 54 (100).

2,2-Dicyano-3-phenylpropionitrile (4)<sup>[18]</sup> was synthesized according to the procedure used for the preparation of 2. The crystalline crude product was recrystallized from ethanol and sublimed in vacuo several times to remove any traces of solvent. Yield of 4 51%; mp  $138^\circ\text{C}$  (ref.<sup>[18]</sup> 64.5%; mp  $140\text{--}141^\circ\text{C}$ ). GC: no impurity  $\geq 0.001\%$ . –  $^1\text{H NMR}$  ( $\text{CDCl}_3/400 \text{ MHz/TMS}$ ):  $\delta = 3.65$  (s, 2H,  $\text{CH}_2$ ), 7.48 (m, 5H, ArH). –  $^{13}\text{C NMR}$  ( $\text{CDCl}_3/100 \text{ MHz/TMS}$ ):  $\delta = 30.63$  [ $\text{C}(\text{CN})_3$ ], 44.13 [ $\text{CH}_2\text{C}(\text{CN})_3$ ], 107.60 (CN), 128.56 (ArC), 129.56 (ArC), 130.40 (ArC). – IR (KBr):  $\tilde{\nu} = 3040 \text{ cm}^{-1}$ , 3030, 2960, 2930, 2200, 1570, 1480, 1440, 1430. – MS (70 eV),  $m/z$  (%): 181 (10), 91 (100), 65 (16), 51 (11), 39 (12).

2-Butyl-2-methylhexanenitrile (5): The available substance<sup>[30]</sup> was purified by using a spinning band column, bp  $64^\circ\text{C}/3 \text{ Torr}$  (ref.<sup>[30]</sup>  $94^\circ\text{C}/12 \text{ Torr}$ ). GC: no impurity  $\geq 0.001\%$ . –  $^1\text{H NMR}$  ( $\text{CDCl}_3/400 \text{ MHz/TMS}$ ):  $\delta = 0.95$  (t, 6H,  $J = 8 \text{ Hz}$ ,  $\text{CH}_3\text{CH}_2$ ), 1.30 [s, 3H,  $\text{CH}_3\text{C}(\text{CN})$ ], 1.30–1.60 (m, 12H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ). –  $^{13}\text{C NMR}$  ( $\text{CDCl}_3/100 \text{ MHz/TMS}$ ):  $\delta = 13.89$  ( $\text{CH}_3\text{CH}_2$ ), 22.84 ( $\text{CH}_3\text{CH}_2$ ), 24.03 [ $\text{CH}_3\text{C}(\text{CN})$ ], 26.98 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 36.70 [ $\text{C}(\text{CN})$ ], 39.22 [ $\text{CH}_2\text{C}(\text{CN})$ ], 124.75 (CN). – IR (film):  $\tilde{\nu} = 2950 \text{ cm}^{-1}$ , 2930, 2205, 1450, 1440. –  $\text{C}_{11}\text{H}_{21}\text{N}$  (167.3)<sup>[30]</sup>: calcd. C 78.97, H 12.65, N 8.37; found C 78.28, H 12.91, N 8.61.

2,2-Dimethylpentanenitrile (6): The available substance<sup>[30]</sup> was purified by using a spinning band column, bp  $60^\circ\text{C}/40 \text{ Torr}$  (ref.<sup>[30]</sup>

38–40°C/18 Torr). GC: no impurity  $\geq 0.001\%$ . –  $^1\text{H}$  NMR ( $\text{CDCl}_3/400\text{ MHz/TMS}$ ):  $\delta = 0.98$  (3H, m,  $\text{CH}_3\text{CH}_2$ ), 1.32 [6H, s,  $\text{CH}_3\text{C}(\text{CN})$ ], 1.50 (4H, M,  $\text{CH}_2\text{CH}_2$ ). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/100\text{ MHz/TMS}$ ):  $\delta = 14.08$  ( $\text{CH}_3\text{CH}_2$ ), 18.59 ( $\text{CH}_3\text{CH}_2$ ), 26.71 [ $\text{CH}_3\text{C}(\text{CN})$ ], 32.40 [ $\text{C}(\text{CN})$ ], 43.32 [ $\text{CH}_2\text{C}(\text{CN})$ ], 125.25 (CN). – IR (film):  $\tilde{\nu} = 2955\text{ cm}^{-1}$ , 2940, 2900, 2840, 2210, 1450, 1380, 1360. –  $\text{C}_7\text{H}_{13}\text{N}$  (111.2) $^{[30]}$ : calcd. C 75.61, H 11.79, N 12.60; found C 75.83, H 11.60, N 12.63.

**2-Methylbutyronitrile (7)** was prepared as described in the literature $^{[31]}$  by refluxing 46.0 g of 2-chlorobutane (500 mmol) and 30.0 g of sodium cyanide in 150 ml of DMSO [*DANGER, the solution can penetrate through the skin*]. The reaction mixture was poured on ice/water and extracted several times with diethyl ether. The combined organic layers were dried with  $\text{Na}_2\text{SO}_4$ . After the solvent had been removed the crude product was purified by using a spinning band column; yield of **7** 20.5 g (50%), bp 123°C (ref. $^{[31]}$  64%, bp 123.5°C). GC: no impurity  $\geq 0.001\%$ . –  $^1\text{H}$  NMR ( $\text{CDCl}_3/60\text{ MHz/TMS}$ ):  $\delta = 1.1$ , (t, 3H,  $J = 7.0\text{ Hz}$ ,  $\text{CH}_3\text{CH}_2$ ), 1.3 (d, 3H,  $J = 7.0\text{ Hz}$ ,  $\text{CH}_3\text{CHCN}$ ), 1.7 (quint, 2H,  $J = 7\text{ Hz}$ ,  $\text{CH}_2\text{CH}_2$ ), 2.7 (sext, 1H,  $J = 7\text{ Hz}$ ,  $\text{CH}-\text{CN}$ ). – IR (KBr):  $\tilde{\nu} = 3000\text{ cm}^{-1}$ , 2850, 2240, 1455, 1380.

**2-Cyano-3-methyl-3-(4-nitrophenyl)butyronitrile (9b)**: To 10.0 g (540 mmol) of 2-cyano-3-methyl-3-phenylbutyronitrile (**9a**) $^{[9]}$  a mixed nitrating acid of 5.4 ml of nitric acid (65%) and 6.5 ml of concentrated sulfuric acid was added at 0°C. After pouring of the reaction mixture on ice the aqueous layer was extracted several times with diethyl ether. The combined organic layers were dried with  $\text{Na}_2\text{SO}_4$ . The solvent was removed, and the crude product was recrystallized several times from dichloromethane/light petroleum (30/50) (2:1). The substance was dried in vacuo to remove any traces of solvent to constant weight; yield of **9b** 6.9 g (55%), mp 109°C. GC: purity level  $\geq 95\%$ ; byproduct 2-cyano-3-methyl-3-(2-nitrophenyl)butyronitrile. –  $^1\text{H}$  NMR ( $\text{CDCl}_3/250\text{ MHz}$ ):  $\delta = 1.75$  (s, 6H,  $\text{CH}_3$ ), 3.88 [s, 1H,  $\text{CH}(\text{CN})_2$ ], 7.60 (d, 2H,  $J = 8\text{ Hz}$ , ArH), 8.30 (d, 2H,  $J = 8\text{ Hz}$ , ArH). – IR (KBr):  $\tilde{\nu} = 3045\text{ cm}^{-1}$ , 3335, 2980, 2960, 2945, 2240, 1585, 1520. – MS (70 eV),  $m/z$  (%): 230 (58), 229 (6), 164 (72), 73 (100).

**2,2-Dicyano-3-methyl-3-(4-nitrophenyl)butyronitrile (10b)**: To a suspension of 1.13 g (47.0 mmol) of NaH in 50 ml of THF a solution of 5.35 g (23.3 mmol) of **9b** in 70 ml of THF was added. The mixture was cooled to 0°C, and a solution of 9.91 g (93.5 mmol) of cyanogen bromide in 70 ml of THF was added rapidly. After warming up to 25°C the solution was filtered to remove NaBr. After evaporation of the solvent the raw product was purified by several recrystallizations from 1,2-dichloroethane/light petroleum (30/50). The solvents were removed from the finely powdered substance in vacuo to constant weight; yield of **10b** 1.88 g (32%); mp 144°C (dec.). GC: no impurity  $\geq 0.001\%$ . –  $^1\text{H}$  NMR ( $\text{CDCl}_3/250\text{ MHz}$ ):  $\delta = 1.90$  (s, 6H,  $\text{CH}_3$ ), 7.8 (d, 2H,  $J = 8\text{ Hz}$ , ArH), 8.4 (d, 2H,  $J = 8\text{ Hz}$ , ArH). – IR (KBr):  $\tilde{\nu} = 3030\text{ cm}^{-1}$ , 2085, 2220, 1590, 1510. – MS (70 eV),  $m/z$  (%): 255 (20), 254 (4), 164 (100). –  $\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_2$  (254.3): calcd. C 61.40, H 3.96, N 22.03; found C 60.91, H 3.95, N 21.88.

**9-(Dicyanomethyl)-9-methylfluorene (9c)**: To 0.12 g (5.0 mmol) of magnesium in 10 ml of diethyl ether a solution of 0.38 ml (6.0 mmol) of methyl iodide in 10 ml of diethyl ether was added. To this solution 1.00 g (4.4 mmol) of **8b** $^{[32]}$  was added in small portions. Vigorous stirring and addition of glass beads during the addition of **8b** increased the velocity of the conversion. The reaction mixture was poured onto an aqueous ammonium chloride solution and then extracted several times with dichloromethane. The combined organic layers were dried with  $\text{MgSO}_4$ . Purification was per-

Table 8. Equilibrium vapour pressures of the alkyl-substituted tricyanomethyl compounds **2–7** determined by the method of transference

	$T$ <sup>[a]</sup> [K]	$m_{\text{cond}}$ <sup>[b]</sup> [mg]	$N_2$ <sup>[c]</sup> [l]	Flow [l ( $N_2$ ) $h^{-1}$ ]	$T_{\text{cond}}$ [K]	$p'$ <sup>[d]</sup> [Torr]	
<b>2</b>	293.2	3.09	5.891	1.86	243	0.0930	
	298.2	4.17	4.618	1.86	243	0.160	
	303.2	3.90	2.678	1.86	243	0.258	
	308.1	5.95	2.657	1.86	243	0.397	
	313.2	4.97	1.317	1.86	243	0.668	
	318.2	8.24	1.380	1.86	243	1.06	
	323.2	8.70	0.962	1.86	243	1.60	
	328.2	8.75	0.651	1.86	243	2.38	
	333.2	6.55	0.326	1.86	243	3.56	
	<b>3</b>	288.2	1.07	2.058	1.96	243	0.0665
293.2		1.36	1.650	1.96	243	0.105	
298.3		1.61	1.272	1.98	243	0.161	
303.3		1.27	0.659	1.98	243	0.243	
308.3		1.44	0.511	1.98	243	0.356	
313.2		1.55	0.380	1.98	243	0.515	
318.2		2.84	0.479	1.98	243	0.749	
323.2		1.37	0.164	1.98	243	1.06	
<b>4</b>		318.2	1.25	48.28	1.82	268	0.00266
		323.2	1.70	37.16	1.82	268	0.00469
	323.2	1.52	37.00	1.82	293	0.00432	
	328.3	1.50	18.71	1.82	268	0.00821	
	328.2	2.15	29.01	1.82	293	0.00772	
	333.3	1.25	9.23	1.82	268	0.0139	
	333.2	1.10	9.10	1.82	293	0.0125	
	338.2	1.41	6.37	1.82	268	0.0228	
	343.2	1.36	3.91	1.82	293	0.0359	
	348.2	1.56	2.750	1.82	293	0.0585	
	358.2	1.77	1.183	1.82	293	0.154	
	363.2	2.33	0.965	1.82	293	0.248	
	368.2	2.44	0.666	1.82	293	0.376	
	373.2	1.83	0.333	1.82	293	0.563	
	378.3	1.77	0.213	1.82	293	0.851	
383.3	1.75	0.151	1.82	293	1.19		
388.3	2.19	0.122	1.82	293	1.85		
<b>5</b>	298.2	8.11	12.21	1.83	243	0.0742	
	303.1	5.59	5.910	1.83	243	0.105	
	308.2	5.91	4.080	1.83	243	0.161	
	313.1	6.32	3.020	1.83	243	0.233	
	318.3	6.48	2.070	1.83	243	0.349	
	323.1	5.71	1.341	1.83	243	0.474	
	328.2	5.74	0.946	1.83	243	0.676	
	333.2	4.48	0.534	1.83	243	0.934	
	338.2	3.77	0.335	1.83	243	1.25	
	<b>6</b>	273.8	5.42	1.114	1.96	243	0.880
278.6		5.88	0.819	1.96	243	1.27	
283.4		6.85	0.654	1.96	243	1.82	
288.3		7.37	0.491	1.96	243	2.58	
293.2		6.73	0.328	1.96	243	3.50	
298.2		7.46	0.261	1.96	243	4.85	
303.2		6.94	0.181	1.96	243	6.49	
<b>7</b>	273.6	12.4	0.972	1.76	243	3.21	
	278.5	13.5	0.737	1.76	243	4.47	
	283.3	15.0	0.589	1.76	243	6.10	
	288.3	15.5	0.442	1.76	243	8.28	
	293.2	13.7	0.295	1.76	243	10.8	
	298.2	15.2	0.235	1.76	243	14.9	
	303.2	14.0	0.163	1.76	243	19.8	
	308.1	11.6	0.103	1.76	243	25.8	
313.4	8.92	0.058	1.76	243	35.2		

<sup>[a]</sup> Temperature  $T$  of measurement. – <sup>[b]</sup> Mass condensed at  $T_{\text{cond}}$ . – <sup>[c]</sup> Volume of  $N_2$  at standard conditions. – <sup>[d]</sup> Vapor pressure  $p'$ ; 1 Torr = 0.75 mbar.



Table 9. Densities, heat capacities, and expansion coefficients for 2–7 and for the auxiliary compounds oil, polyethylene, and cotton thread

Substance	$d$ (293 K) [g cm <sup>-3</sup> ]	expansion coefficient [a] [10 <sup>-6</sup> K <sup>-1</sup> ]	$C_D$ (298 K) [d] [J g <sup>-1</sup> K <sup>-1</sup> ]
<b>2</b>	1.01	0.1	0.315
<b>3</b>	0.96	1.0	0.335
<b>4</b>	1.12	0.1	0.386
<b>5</b>	0.80	1.0	0.514
<b>6</b>	0.77	1.0	0.525
<b>7</b>	0.78	1.0	0.777
oil [b]	0.88	1.0	0.830
cottonthread [c]	1.50	0.1	1.67
polyethylene [d]	0.92	0.1	2.53

[a] Estimated. – [b] CH<sub>1.94</sub> Δ $u_c^0$  = -45996.68 ± 7.15 J g<sup>-1</sup>. – [c] CH<sub>1.774</sub>O<sub>0.887</sub> Δ $u_c^0$  = -16945.2 ± 4.2 J g<sup>-1</sup>. – [d] CH<sub>1.93</sub> Δ $u_c^0$  = -46372.2 ± 2.8 J g<sup>-1</sup>.

formed by recrystallization from ethanol; yield of **9c** 0.86 g (80%), mp 97°C. GC: no impurity ≥ 0.1%. – <sup>1</sup>H NMR (CDCl<sub>3</sub>/250 MHz): δ = 1.82 (s, 3H, CH<sub>3</sub>), 3.95 [s, 1H, CH(CN)<sub>2</sub>], 7.40 (m, 4H, ArH), 7.73 (m, 4H, ArH). – IR (KBr):  $\tilde{\nu}$  = 3045 cm<sup>-1</sup>, 2970, 2960, 2920, 2880, 2250, 1600, 1480, 1375, 1300. – MS (70 eV),  $m/z$  (%): 244 (16) 179 (100). – C<sub>17</sub>H<sub>12</sub>N<sub>2</sub> (244.3): calcd. C 83.58, H 5.00, N 11.46; found C 82.84, H 4.95, N 11.31.

**9-Methyl-9-(tricyanomethyl)fluorene (10c)**: To a suspension of 60 mg (2.4 mmol) of NaH in 10 ml of THF a solution of 530 mg (2.1 mmol) of **9c** in 10 ml of THF was added. The red solution was cooled to 0°C, and a solution of 260 mg (2.5 mmol) of cyanogen bromide in 10 ml of THF was added rapidly. After warming up to 25°C the solution was filtered to remove NaBr. After evaporation of the solvent the raw product was purified by chromatography on silica gel using cyclohexane/ethyl acetate (2:1). The thermolabile product was recrystallized from 1,2-dichloromethane/light petroleum (30:50). The solvents were removed from the finely powdered substance in vacuo to constant weight; yield of **10c** 100 mg (17%), mp 130°C (dec.). GC (100°C isotherm): no impurity ≥ 2.5%. – <sup>1</sup>H NMR (CDCl<sub>3</sub>/250 MHz): δ = 2.03 (s, 3H, CH<sub>3</sub>), 7.44 (m, 2H, ArH), 7.56 (m, 2H, ArH), 7.82 (m, 4H, ArH). – IR (KBr):  $\tilde{\nu}$  = 3045 cm<sup>-1</sup>, 2970, 2960, 2920, 2880, 2250, 1600, 1480, 1375, 1300. – MS (70 eV),  $m/z$  (%): 269 (5), 180 (17), 179 (100) 178 (47), 177 (10), 176 (14), 152 (11), 90 (11), 89 (22), 88 (11), 76 (16), 43 (16). – C<sub>18</sub>H<sub>11</sub>N<sub>3</sub> (269.3): calcd. C 80.28, H 4.12, N 15.60; found C 79.89, H 3.47, N 15.04.

**9-Methoxy-9-methylfluorene (13)**: To 0.134 g (5.60 mmol) of NaH in 20 ml of THF a solution of 1.10 g (5.60 mmol) of 9-hydroxy-9-methylfluorene<sup>[33]</sup> was added. After 1 h at room temp. 0.87 g (6.10 mmol) of iodomethane in 20 ml of THF was added. The reaction mixture was poured on 50 ml of water and 50 ml of diethyl ether. The organic layer was separated, and the aqueous layer was extracted several times with diethyl ether. The combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent the crude product was recrystallized from ethanol; yield of **13** 0.93 g (79%), mp 87°C. GC: no impurity ≥ 0.1%. – <sup>1</sup>H NMR (CDCl<sub>3</sub>/250 MHz): δ = 1.67 (s, 3H, CH<sub>3</sub>), 2.75 (s, 3H, OCH<sub>3</sub>), 7.33 (m, 4H, ArH), 7.47 (m, 2H, ArH), 7.65 (m, 4H, ArH). – IR (KBr):  $\tilde{\nu}$  = 3045 cm<sup>-1</sup>, 3010, 2950, 2900, 2870, 2790, 1430, 1420. – MS (70 eV),  $m/z$  (%): 210 (28), 195 (68), 179 (100), 165 (7), 152 (20).

**Enthalpy of Combustion**: For measuring the enthalpies of combustion of **2**, **3**, **4**, **5**, **6**, and **7** an isoperibolic macrocalorimeter<sup>[34]</sup> with stirred water bath was used. The substances were pressed into

tablets of ≈300 mg weight or filled into polyethylene capsules which were burned in the calorimeter. The detailed procedure has been described previously<sup>[21]</sup>. The heat equivalent of the calorimeter was obtained with a standard reference sample of benzoic acid (sample SRM 39i, National Bureau of Standards). The values found are  $\epsilon(J) = 25105.03 \pm 3.39$  (0.0135%) J K<sup>-1</sup> for **2**, **3**, and **4** and  $25088.10 \pm 1.05$  (0.0042%) for **5**, **6**, and **7**. The energy for ignition was determined to be 1.46 J. – The purities of the samples were controlled by GC and showed no impurity ≥ 0.001%. Hence, sample **3** was burned with water (0.137% Fischer titration; correction was made). The densities of the compounds **2** and **4** were determined by keeping these in suspension in solutions of NaBr of known density (Table 9). The densities of **3**, **5**, **6**, and **7** were determined with a pycnometer. The specific heat capacities were measured with DSC (Table 9). For the conversion of the data to standard conditions conventional procedures<sup>[35]</sup> were used. The results of the different combustion experiments are listed in Tables 6 and 7.

**Enthalpy of Fusion**: The enthalpies of fusion of **2** and **4** were determined by DSC. The purities of **2** and **4** were controlled and compared with the values of GC. They were ≥ 99.99% (DSC).

**Enthalpy of Sublimation/Vaporization**: The enthalpies of sublimation Δ $H_{\text{sub}}^0$  of **2** and **4** and the enthalpies of vaporization Δ $H_{\text{vap}}^0$  of **3** and **5**–**7** were determined by means of the method of transference in a saturated N<sub>2</sub> stream<sup>[24]</sup>. The substances were mixed with glass beads and filled in a thermostated U tube. At several different temperatures a slow nitrogen stream was passed through the U tube, and the transported amount of material was condensed in a second cooled U tube. Its mass was determined by GC analysis after addition of an internal standard, and the apparent vapor pressure was calculated thereof. The obtained data are listed in Table 8.

$$\Delta H_{\text{sub}}^0 = -R[\ln(p')/dT^{-1}] \quad (9)$$

The enthalpies of sublimation or vaporization were calculated from eq. (9) (with  $R$  = gas constant,  $p'$  = apparent vapor pressure,  $T$  = temperature), considering the vapor pressure at condensation temperature in an iterative procedure<sup>[36]</sup>. The values are recorded in Tables 2 and 8.

**Product Analysis**: An 0.1 M solution of **10a**, **10b**, or **10c** in *tert*-butylbenzene, benzene or in other experiments in polar solvents (THF, methanol) were heated under N<sub>2</sub> in sealed glass ampoules at 120–180°C up to 1 h. The formed reddish precipitate was removed by filtration, and the filtrates were analyzed by GC using an internal standard. The products were identified by GC/MS and comparison with authentic samples<sup>[12]</sup>.

**Kinetic Measurements**: The samples were prepared by mixing N<sub>2</sub>-saturated stock solutions of TEMPO and **10c** in *tert*-butylbenzene, and O<sub>2</sub> was removed completely. The sample was brought into the EPR cavity at room temp., and the maximum of the overmodulated (1G) central peak of the TEMPO signal was monitored (see Figure 1). The sample was heated to the reaction temp., and the signal showed a rapid decrease due to volume expansion and to the correlation between signal height and temperature following the Curie law. In an independent experiment using only the TEMPO stock solution, it was shown that this behavior is reversible upon heating and cooling the probe. After about 25 s ( $t_1$ ) the decrease of the signal became slower, and a linear correlation between signal height and time was observed up to ≈90% conversion (decrease of TEMPO). From its slope the values for  $d[\text{TEMPO}]/dt$ , were obtained and the rate constant (Table 1) was calculated by using eq. (3). The fractional decomposition during heating up to  $t_1$  was  $f_{\text{dec}} = 1.00$  (365.65 and 376.15 K), 0.99 (386.75 K), 0.98 (397.35

K), and 0.97 (402.25 K). The average concentration of **10c** during the kinetic run was  $c_{\text{Dimer}}(t_{\text{av.}}) = [c_{\text{Dimer}}(t_1) + c_{\text{Dimer}}(\text{end})]/2$ . The concentration  $c_{\text{Dimer}}(\text{end})$  of **10c** for complete conversion of TEMPO was  $c_{\text{Dimer}}(\text{end}) = c_{\text{TEMPO}}/(\text{conversion}(\%) \cdot 0.115 \cdot 2)$  (see Table 1).

*Force-Field Calculations* were carried out with Allinger's MM2 program<sup>[37]</sup>. The properties of the tricyanomethyl radical and the alkyl-substituted dicyanomethyl radical were calculated with the enhanced MM2 parameters described in the literature<sup>[29]</sup>. For both types of planar<sup>[8]</sup> radicals we used a preferred angle for NC–C–CN of 120 and a force constant of 0.47<sup>[37]</sup>. The calculated values for the strain enthalpies (MM2) and dipolar interactions are given in Table 10.

Table 10. Strain enthalpies  $H_{\text{sp}}$  and dipolar interactions from MM2 force-field calculations

	$H_{\text{sp}}$ (MM2) [kJ mol <sup>-1</sup> ]	Dipolar interaction (MM2) [kJ mol <sup>-1</sup> ]
HC(CN) <sub>3</sub>	79.7 [a]	82.5
9-methylfluorene	42.8 [a]	0.0
<b>10c</b>	134.1 [a]	93.9
Dimethylmalononitrile C[C <sub>2</sub> (CN) <sub>2</sub> ]	30.0	27.9 [b]
1,1-Dicyanoethyl radical C[C(CN) <sub>2</sub> ]	24.0	16.3 [b]
2,2-Dicyanopropionitrile (2) C[C(CN) <sub>3</sub> ]	83.6	83.1 [b]
Tricyanomethyl radical (1) C-[CN] <sub>3</sub>	75.2	69.7 [b]

[a] Strain enthalpies of the asymmetrical dimer **10c** and the corresponding monomers HC(CN)<sub>3</sub> and 9-methylfluorene used for the determination of the strain of dissociation  $D'_s$  (**10c**). – [b] Dipolar interactions of geminal cyano groups in aliphatic cyano compounds and in cyano-substituted radicals.

- [1] F. Welle, S. P. Verevkin, M. Keller, H.-D. Beckhaus, C. Rüchardt, *Chem. Ber.* **1994**, *127*, 697–710.  
 [2] R. Schulze, H.-D. Beckhaus, C. Rüchardt, *Chem. Ber.* **1993**, *126*, 1031–1038.  
 [3] [3a] See ref.<sup>[4]</sup>. – [3b] For a review see: C. Rüchardt, H.-D. Beckhaus, *Top. Curr. Chem.* **1985**, *130*, 1–22. – [3c] K. Rakus, S. P. Verevkin, J. Schätzer, H.-D. Beckhaus, C. Rüchardt, *Chem. Ber.* **1994**, *127*, 1095–1103.  
 [4] J. Pakusch, H.-D. Beckhaus, C. Rüchardt, *Chem. Ber.* **1991**, *124*, 1191–1198.  
 [5] H. K. Hall, *J. Am. Chem. Soc.* **1971**, *93*, 140–145.  
 [6] G. Stridh, S. Sunner, CH. Svensson, *J. Chem. Thermodyn.* **1997**, *9*, 1005–1010.  
 [7] [7a] M. Meier, B. Dogan, H.-D. Beckhaus, C. Rüchardt, *N. J. Chem.* **1987**, *11*, 1–6. – [7b] H.-D. Beckhaus, B. Dogan, J. Pakusch, S. P. Verevkin, C. Rüchardt, *Chem. Ber.* **1990**, *123*, 2153–2159.

- [8] R. A. Kaba, K. U. Ingold, *J. Am. Chem. Soc.* **1976**, *98*, 523–526.  
 [9] S. Trofimenko, E. L. Little, H. F. Mower, *J. Org. Chem.* **1962**, *27*, 443–438.  
 [10] D. T. Mowry, *J. Am. Chem. Soc.* **1945**, *67*, 1050–1051.  
 [11] F. S. Prout, E. P.-Y. Huang, R. J. Hartman, C. J. Korpics, *J. Am. Chem. Soc.* **1954**, *76*, 1911–1913.  
 [12] K. Rakus, Dissertation, in preparation.  
 [13] H. Hirota, T. Mitsuhashi, *Chem. Lett.* **1990**, 803–806.  
 [14] H.-D. Beckhaus, J. Schoch, C. Rüchardt, *Chem. Ber.* **1977**, *110*, 878–895.  
 [15] M. Newcomb, *Tetrahedron* **1993**, *49*, 1151–1176.  
 [16] For the method described (using UV-Vis spectroscopy) see: H.-D. Beckhaus, Dissertation, University of Freiburg, **1975**, and ref.<sup>[1]</sup>.  
 [17] R. G. Cvetanovic, D. L. Singleton, *Int. J. Chem. Kinetics* **1977**, *9*, 481–488.  
 [18] M. B. Frankel, A. B. Amster, E. R. Wilson, M. McCormick, M. McEachern, *Adv. Chem. Ser.* **1965**, *54*, 108–117.  
 [19] E. Cox, A. Fontaine, *Bull. Soc. Chim. Fr.* **1954**, 948–950.  
 [20] *Determination of Purity Using Recording Differential Calorimetry*, Analytentechnische Berichte 45, Bodenseewerk Perkin-Elmer & Co. GmbH, Überlingen, **1976**.  
 [21] H.-D. Beckhaus, C. Rüchardt, M. Smisek, *Thermochim. Acta* **1984**, *79*, 149–159.  
 [22] S. Lotz, G. Gatow, *Z. Anorg. Allg. Chem.* **1992**, *611*, 134–136.  
 [23] H.-D. Beckhaus, G. Kratt, K. Lay, J. Geiselmann, C. Rüchardt, B. Kitschke, H. J. Lindner, *Chem. Ber.* **1980**, *113*, 3441–3445.  
 [24] J. D. Cox, G. Pilcher in *Thermochemistry of Organic Compounds*, Academic Press, London, **1970**.  
 [25] M. A. Flamm-ter Meer, H.-D. Beckhaus, C. Rüchardt, *Thermochim. Acta* **1984**, *80*, 81–89.  
 [26] A. Xu-Wu, M. Mansson, *J. Chem. Thermodyn.* **1983**, *15*, 287–293.  
 [27] R. Winiker, H.-D. Beckhaus, C. Rüchardt, *Chem. Ber.* **1980**, *113*, 3456–3476.  
 [28] W. Barbe, H.-D. Beckhaus, C. Rüchardt, *Chem. Ber.* **1983**, *116*, 1042–1057.  
 [29] A. Peyman, E. Hickl, H.-D. Beckhaus, *Chem. Ber.* **1987**, *120*, 713–725.  
 [30] H. Langhals, C. Rüchardt, *Chem. Ber.* **1981**, *114*, 3831–3854.  
 [31] L. Friedman, H. Shechter, *J. Org. Chem.* **1960**, *25*, 877–879.  
 [32] R. Schenck, H. Finken, *Liebigs Ann. Chem.* **1928**, *462*, 267–283.  
 [33] F. Ullmann, R. v. Wurstenberger, *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 4105–4112.  
 [34] S. Sunner in *Experimental Chemical Thermodynamics* (Eds.: S. Sunner, M. Mansson), Pergamon Press, Oxford, **1979**.  
 [35] W. N. Hubbard, D. W. Scott, G. Waddington in *Combustion Calorimetry* (Ed.: F. D. Rossini), Interscience Publishers, New York, **1956**, p. 75–127.  
 [36] E. Hickl, H.-D. Beckhaus, Universität Freiburg, **1980**. The program may be obtained from the authors on request.  
 [37] N. L. Allinger, *J. Am. Chem. Soc.* **1977**, *99*, 8127–8134.  
 [38] J. Timmermans, F. Martin, *J. Chem. Phys.* **1928**, *25*, 411;  $\alpha_T(n\text{-butylbenzene}) = 960 \cdot 10^{-6} \text{ grd}^{-1} (0\text{--}30^\circ\text{C})$ .  
 [39] G. Leroy, M. Sana, C. Wilante, *J. Mol. Struct.* **1989**, *198*, 159–173.

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