Substituent Effects on the C–C Bond Strength,  $20^{[1]}$  Geminal Substituent Effects,  $14^{[2]}$ 

# Stabilization of the Cyano(dimethylamino)methyl Radical – Synergistic Effect Due to Interaction between $\alpha$ -Amino and $\alpha$ -Cyano Groups on the Radical Stabilization Energy<sup> $\ddagger$ </sup>

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The thermolysis reactions of **3a** and **2a**, **b** were studied over a temperature range of 40 °C and the activation parameters were determined. They were compared with the activation parameters of structurally comparable hydrocarbons of similar strain in order to obtain the radical stabilization enthalpies RSEs of the cyano(dimethylamino)methyl radical **1a**. For this comparison the geminal interaction enthalpies of the cyano and the dimethylamino groups in the ground state had to be determined for the series of amino nitriles **4a**-**4c** and **4j**-**4n** by thermochemical methods. The geminal interaction in the ground state varies between -0.6 kcal/mol stabilization in **4a** and a destabilization of +10.7 and +7.0 kJ mol<sup>-1</sup>

Previously we developed methods for determining stabilization enthalpies of substituted alkyl radicals generated by homolytic C–C bond cleavage reactions<sup>[3]</sup>.

For S = alkyl the activation enthalpy  $\Delta H^{\pm}$ , which corresponds to the C–C bond dissociation enthalpy, decreases with increasing branching at the central carbon atoms (C<sub>q</sub> < C<sub>t</sub> < C<sub>s</sub>) and with increasing loss of strain enthalpy  $H_{\rm S}$  during the dissociation process<sup>[3]</sup>. When S is a functional group, the quality of its interaction with the single electron of the radical center by resonance also affects the bond dissociation enthalpy. C–C bond dissociation enthalpies may be predicted, therefore, when radical stabilization enthalpies RSE are known and vice versa.

More recently, we addressed the question of measuring the RSEs of geminally disubstituted alkyl radicals SS'RC<sup>•</sup> by using the same procedure. Is the substituent effect on the RSE in this type of radicals additive, less than additive or more than additive if compared with the results for the monosubstituted radicals  $SR_2C^{\bullet}$  and  $S'R_2C^{\bullet}$  (R = Alkyl)?

Viehe<sup>[4,5]</sup> originally had proposed a more than additive, e.g. synergistic stabilization, when a capto substituent (e.g. C=O) and a dative substituent (e.g. OMe, SMe) are comfor secondary and tertiary  $\alpha$ -dialkylaminonitriles, respectively. A synergistic (i.e. more than additive) stabilization enthalpy of 26 kJ mol<sup>-1</sup> of **1a** was found in contrast to predictions in the literature. This stabilization is interpreted by conjugation between the substituents, which are separated by the radical center.



$$R \xrightarrow{S \ S}_{S' \ S'} R \xrightarrow{S}_{R} 2 \xrightarrow{S}_{R} 3'$$

bined. In contrast, two capto or two dative substituents were expected to interact antagonistically, i.e. to stabilize a radical center less than additively<sup>[4,5]</sup>.

For a reliable interpretation of the bond dissociation enthalpies of this type not only the strain enthalpies of the radicals and their precursors had to be determined (usually by MM2 calculations) but also the electronic interaction of the substituents in the radical precursor (ground-state effect) had to be taken into account. For this reason geminal substituent effects for many pairs of geminal substituents in the ground state were determined from their enthalpies of formation  $\Delta H_{\rm f}^0$ , which were measured by thermochemical methods.

In our early work we found that, in general, the effect of geminal substituents on the RSE of alkyl radicals is an additive one<sup>[3]</sup>. As examples the  $\alpha$ -cyano- $\alpha$ -methoxylakyl radicals are cited<sup>[6,7]</sup>. More recently, however, we found examples in which the stabilizing effect of geminal substituents is synergistic<sup>[8,9,10]</sup>, i.e. more than additive. In the frame of resonance theory and "resonance structures" the requirement for a synergistic interaction was that a dative dialkylamino and a capto carbonyl substituent interacted with

**FULL PAPER** 

each other. This captodative effect, accordingly, was not interpreted by a typical radical-stabilizing interaction but rather by a homoamide conjugation interaction between the carbonyl and the amino group which is similar to the amide resonance in acid amides.



Consequently, the question arose whether geminal amino and cyano groups also give rise to a synergistic extra stabilization like the homoamide resonance or not. Recently, Leroy et al.<sup>[11]</sup>, who used computational methods, reported on a slightly antagonistic effect of -2.9 kJ mol<sup>-1</sup> for the geminal amino-cyano substitution pattern. In another theoretical investigation, Pasto<sup>[12]</sup> found a slight synergistic effect of 4.6 kJ mol<sup>-1</sup> for the geminal amino-cyano substitution of radicals. In both publications the substituent effect of the amino and cyano substitution pattern was nearly additive.



To determine the RSE of the cyano(dimethylamino)methyl radical 1a we investigated the influence of the amino and cyano substituent on the homolytic dissociation of the central C-C bonds of the unsymmetrically substituted ethanes 2a and 2b and of the symmetrical dimer 3a of 1a.

#### **Synthesis**

The dimer **3a** was obtained either by photochemical dimerization of dimethylaminoacetonitrile **4a** with di-*tert*-butyl peroxide (DTBP) in benzene or by the reaction of an aqueous solution of glyoxal **5** with KCN and dimethylammonium hydrochloride. While the first procedure provided a *meso/DL* mixture of **3a**, pure crystalline *meso-***3a** was obtained by the latter. The configuration of *meso-***3a** was determined by X-ray structure analysis<sup>[13]</sup>.



The unsymmetrical ethanes 2a and 2b were prepared from the respective aldehydes 6 by treatment with dimethylammonium hydrochloride and KCN in water. The  $\alpha$ -dialkylaminonitriles 4, which were required for the thermochemical measurements, were prepared in the same way according to literature procedures<sup>[14]</sup> and purified by distillation or recrystallization.



### Kinetics

First the kinetics of the homolytic C–C bond cleavage reaction of *meso-3a* was determined by following the thermal isomerization of *meso-3a* to DL-3a in [D<sub>6</sub>]benzene between 180 and 216 °C by <sup>1</sup>H-NMR spectroscopy. The signals of the protons of the dimethylamino groups of the two diastereomers were used to measure the relative concentrations of *meso-* and DL-3a. The kinetic equation for the unimolecular approach to the equilibrium mixture was used<sup>[15]</sup>.



A problem arose because concurrently with the isomerization **3a** slowly eliminated HCN under the reaction conditions to afford *cis*- and *trans*-2,3-bis(dimethylamino)acrylonitrile **7**. The increase of the concentration of **7** was also followed by <sup>1</sup>H-NMR spectroscopy; the dimethylamino protons of both olefins also give rise to signals at different  $\delta$  values (see Table 6). In order to allow for the effect of this side reaction in the kinetics,  $c_0$  in the kinetic equation was, for each reaction time, set equal to  $c_{meso} + c_{DL}$ <sup>[16]</sup>.

$$\ln\{(Kc_{meso} - c_{\rm DL})/Kc_0\} = -(k_1 + k_2)t \tag{1}$$

$$K = k_1 / k_2 \tag{2}$$

From the temperature dependence of the rate constants  $k_1$  and  $k_2$  (Table 7) the activation parameters of the homolytic bond cleavage were calculated (Table 1).

In order to prevent the effect of HCN elimination on the kinetics we investigated the model compounds 2a and 2b in which the absence of a hydrogen atom  $\beta$  to the cyano group makes the elimination impossible. For the determination of the RSE of the title radicals generated by homolytic C-C bond cleavage in the cases, the RSEs of the cumyl radical<sup>[17]</sup> **8a** (35.2 kJ mol<sup>-1</sup>) and the 1,1-diphenylethyl radical<sup>[18]</sup> **8b**  $(46.0 \text{ kJ mol}^{-1})$  have to be taken in consideration. The thermolysis reactions of 2a and 2b were studied in mesitylene containing a 10-fold excess of thiocresol as hydrogen donor. Dimethylaminoacetonitrile 4a and 1,1-diphenylethane were the major products of the thermolysis of 2b; cumene (in the case of 2a) could not be determined by GC because its peak could not be separated from the solvent peak of mesitylene. The rate constants of the thermolysis reactions were determined by following the decrease in concentration of the starting compounds 2. Details are given in the experimental section. From the temperature dependence of the rate constants the activation enthalpies and activation entropies were calculated (Table 1).



Table 1. Activation parameters (in kJ mol<sup>-1</sup>) of the homolytic dissociation of *meso-* and DL-**3a** and **2a**, **b** from kinetic measurements of reaction 1 and  $2^{[a]}$ 

	Solvent	∆H <sup>≢</sup>	∆S <sup>≠[b]</sup>	∆G <sup>≠[c]</sup>	$T_{1h}^{[d]}$
meso-3a	[D <sub>6</sub> ]benzene	168.2 ± 3.8	37.7 ± 8.4	146.9 ± 3.8	198
DL-3a	[D <sub>6</sub> ]benzene	$150.6\pm5.0$	9.6 ± 10.4	$145.6 \pm 5.0$	186
2a	mesitylene/thiocresol	128.9 ± 2.9	-58.6 ± 5.9	$162.8\pm4.2$	220
2b	mesitylene/thiocresol	$152.3\pm8.8$	16.7 ± 18.8	$142.7\pm8.8$	180

<sup>[a]</sup> For the rate constants see Table 7 and Table 8. - <sup>[b]</sup> In J mol<sup>-1</sup> K<sup>-1</sup>. - <sup>[c]</sup> Extrapolated to 300 °C. - <sup>[d]</sup> Temperature in °C with a half-life time of 1 h.

In addition, we attempted to determine the kinetics of the thermal decomposition of 2a and 2b by DSC<sup>[19]</sup> by following the heat flow during heating at a constant rate. For

**2b** only small peaks were obtained and even smaller and insignificant signals for **2a** could be detected. The activation parameters listed in Table 2 for the decomposition of **2b** were obtained by rigorous analysis involving iterative simulation<sup>[19]</sup>. Due to the small overall heat flow the free enthalpies of activation  $\Delta G^{\pm}$  could not be reproducibly split into  $\Delta H^{\pm}$  and  $\Delta S^{\pm}$  (see Table 2). The average value of  $\Delta G^{\pm}$ (139.1 ± 1.7 kJ mol<sup>-1</sup>) is, however, in good agreement with the value found by the GC method (Table 1). It has been shown previously for  $\alpha$ -methoxy- $\alpha$ -cyano alkyl radicals<sup>[20]</sup> and for  $\alpha$ -amino- $\alpha$ -carbonyl alkyl radicals<sup>[8]</sup> that the rates of thermolysis by C–C-cleavage reactions of their dimers do not significantly depend on solvens polarity.

Table 2. Activation parameters of the homolytic bond cleavage of **2b** determined by DSC measurements<sup>[19]</sup> with thiocresol as radical scavenger (in kJ mol<sup>-1</sup>)

	Solvent/Scavenger	ratio	∆H <sup>≢</sup>	∆S <sup>≭[a]</sup>	∆G <sup>≠</sup>	T <sub>1h</sub> [b]
2b	di-n-butyl phthalate/thiocresol	4:1	146.9	10.0	141.0	178
2b	mesitylene/thiocresol	2:1	150.2	16.7	140.6	178
2b	mesitylene/thiocresol	2:1	161.9	41.8	138.1	180
2b	tetralin/thiocresol	2:1	161.1	42.3	136.8	177
	mean values		$155.0 \pm 6.6$	27.7 ± 14.5	139.1 ± 1.7	

<sup>[a]</sup> In J mol<sup>-1</sup> K<sup>-1</sup>. - <sup>[b]</sup> Temperature in °C with a half-life time of 1 h.

#### **Thermochemical Measurements**

Δ

The geminal amino and cyano substituents in  $\alpha$ -amino carbonitriles interact with each other in a synergistic manner<sup>[21]</sup>. The heats of formation  $\Delta H_f^0$  of the amino nitriles, accordingly, cannot be predicted from the known thermochemical increments which were determined independently from amines and nitriles. In order to quantify this synergistic interaction  $\Delta\Delta H$  (eq. 3) the heats of formation  $\Delta H_f^0(g)$  for some gemial amino nitriles **4** were determined thermochemically and compared with the values which were calculated by the group increment procedure. Strain enthalpies  $H_S$  were calculated by MM2 and  $H_S = 2.8$  kJ mol<sup>-1</sup> and 12.6 kJ mol<sup>-1</sup> were obtained for **4j** and **4m**. For all other compounds the calculated strain was negligibly small.

$$\Delta H = \Delta H_{\rm f}^0({\rm g}) - \Sigma \text{ group increments except} CH_{3-n}[{\rm N,CN,C}_{n-1}] \text{ with } n = 1, 2, 3 \quad (3)$$

For the thermochemical measurements samples of  $4\mathbf{a}-\mathbf{c}$ and  $4\mathbf{j}-4\mathbf{n}$  were prepared and purified by distillation or recrystallization (purity  $\geq 99.99\%$ ). Their purity was monitored by GC and that of the solids  $4\mathbf{c}$ ,  $4\mathbf{j}$ ,  $4\mathbf{k}$ ,  $4\mathbf{m}$ , and  $4\mathbf{n}$ by analyzing the melting process by DSC<sup>[22]</sup>.  $\Delta H_{\rm f}^0(1)$  for  $4\mathbf{g}$ is known from the literature<sup>[23]</sup>.

The standard enthalpies of formation for the gas phase  $\Delta H_{\rm f}^0({\rm g})$  were calculated from the standard enthalpies of formation for the condensed phase  $\Delta H_{\rm f}^0({\rm c})$  (liquid or crystalline, average value from four or five measurements, in the case of **4m** from three measurements) and the enthalpies of vaporization  $\Delta H_{\rm V}$  or the enthalpies of sublimation  $\Delta H_{\rm Sub}$  and the enthalpies of fusion  $\Delta H_{\rm m}$  in the case the crystalline compounds. All values refer to standard conditions (see Table 4).

The strain-free increments for the alkanes and monosubstituted alkanes are taken from refs.<sup>[8,24,25]</sup>. The increments

## FULL PAPER

CH<sub>2</sub>[N,CN] for  $4\mathbf{a}-\mathbf{c}$ , CH[N,CN,C] for  $4\mathbf{g}$ , C[N,CN,C<sub>2</sub>] for  $4\mathbf{j}-4\mathbf{k}$ , and CH[N,CN,Ph] for  $4\mathbf{l}-4\mathbf{n}$  were compiled as average values of  $\Delta\Delta H$  (eq. 3) in Table 4. The geminal interaction  $\Delta H_{\text{gem}}$  of an amino and cyano group was calculated from the strain-free group increments of the amino, cyano and amino-cyano compounds by eq. 4.

$$\Delta H_{\text{gem}} = \Delta H_{\text{XY}} - \Delta H_{\text{X}} - \Delta H_{\text{Y}} + \Delta H_{\text{alkyl}}$$
(4)

#### **Results and Discussion**

Table 3. Strain-free increments<sup>[a]</sup> for alkyl-, cyano-, dialkylamino-, and dialkylamino-cyano-substituted carbon atoms and the geminal interaction  $\Delta H_{\text{gem}}$  (in kJ mol<sup>-1</sup>)

	$\Delta H_{alkyl}$ [23]	∆H <sub>cyano</sub> <sup>[24]</sup>	$\Delta H_{amino}$ [8]	∆ <i>H</i> aminocyano	$\Delta H_{gem}^{[b]}$
n	$CH_{3-n}[C_{n+1}]$	CH <sub>3-n</sub> [CN,C <sub>n</sub> ]	$CH_{3-n}[N,C_n]$	$CH_{3-n}[N, CN, C_{n-1}]$	
0	-42.05	= (-42.05)	≡ (-42.05)		
1	-21.46	-18.37	-25.02	-22.5	-0.6
2	-9.04	-7.66	-18.66	-6.6	+10.7
3	-1.26	+6.86	-13.43	+1.7	+7.0
				CH[N,CN,Ph]	
				-9.0	

<sup>[a]</sup> Adjacent atoms in brackets. - <sup>[b]</sup> Eq. 4.

The thermochemical measurements of the amino nitriles 4 reveal the influence of the geminal cyano and amino groups for the different alkylated and phenylated groups. The values of the group increments  $CH_{3-n}[N, CN, C_{n-1}]$ show the typical increase by going from primary to tertiary groups already noted for primary, secondary, and tertiary alkyl groups. Even the differences between the increments of these groups (step size) are similar for the amino nitriles and for the hydrocarbons. A quite different situation was found for the amines (see Table 3) because the comparable differences between the groups (step size) are smaller. The geminal interaction  $\Delta H_{gem}$  (see Table 3) between CN and N for the groups  $CH_{3-n}[N, CN, C_{n-1}]$ , which are calculated by eq. 4, show for n = 1 a slight stabilization of the ground state and for n = 2 and n = 3 a destabilization. With the knowledge of these geminal interactions of the ground state, we were able to deduce the radical stabilization enthalpy RSE of 1a from the kinetic measurements (reactions 1 and 2) after consideration of ground-state effects in the radical precursors. RSE(1a) was calculated by use of eq. 5 for the symmetrical dimers **3a** or by use of eq. 6 for the unsymmetrical compounds **2**.

$$RSE(1a) = \frac{1}{2} \left( \Delta \Delta G_{300\,^{\circ}C}^{\pm} + 0.573 \ \Delta \Delta S^{\pm} \right) - \Delta H_{gem}(CH[N,CN,C]) \quad (5)$$

$$RSE(1a) = \Delta \Delta G_{3000}^{\pm} + 0.573 \ \Delta \Delta S^{\pm} - RSE(8)$$

$$= \Delta H_{\text{gem}}(\text{CH[N,CN,C]}) \quad (6)$$

 $\Delta\Delta G^{\pm}$  and  $\Delta\Delta S^{\pm}$  are the differences in  $\Delta G^{\pm}$  and  $\Delta S^{\pm}$  for the decomposition of **1a** and a tetraalkylethane<sup>[3]</sup> of identical strain of dissociation  $D_{\rm S}$ , or of **2** and a pentaalkylethane<sup>[3]</sup> of identical  $D_{\rm S}$ .  $\Delta H_{\rm gem}(\rm CH[N,CN,C]$  is the geminal ground-state effect of the amino-nitrile substitution pattern (see Table 3). The negative activation entropy of **2a** in Table 1 is somewhat surprising and unusual for a homolytic bond cleavage reaction<sup>[3]</sup>. Therefore, we did not take this value into consideration for the calculation of the RSE of the radical **1a**. The resultant values for RSE(**1a**) are compiled in Table 5.

Table 5. Free enthalpies of activation at 300 °C for the homolytic C-C bond cleavage of 2 and 3 and of alkylethanes of identical strain of dissociation  $D_S$  and the stabilization enthalpies RSE of the radical 1a in kJ mol<sup>-1</sup>

	Ds	∆G <sup>≠</sup> (alkane)	∆G <sup>≠</sup> (aminonitrile)	RSE(1a)
meso-3a	30.4	254.0 <sup>[a]</sup>	$146.9 \pm 3.8$	49.7
DL- <b>3a</b>	28.6	255.4 <sup>[a]</sup>	$145.6 \pm 5.0$	59.1
2b	44.8	234.3 <sup>[b]</sup>	$142.7\pm8.8$	55.0
2b	44.8	234.3 <sup>[b]</sup>	139.1 ± 1.7 <sup>[c]</sup>	52.4
			mean value	$54.1 \pm 3.4$

<sup>[a]</sup>  $\Delta \Delta G_{300^{\circ}C}^{\pm}$  of the thermolysis reaction of a  $C_t - C_t$  alkane of identical strain of dissociation  $D_s$ . – <sup>[b]</sup>  $\Delta \Delta G_{300^{\circ}C}^{\pm}$  of the thermolysis reaction of a  $C_t - C_q$  alkane of identical strain of dissociation  $D_s$ . – <sup>[c]</sup> Average value of  $\Delta G_{300^{\circ}C}^{\pm}$  of **2b** from four DSC measurements.

The mean value for the RSE(1a) is calculated to be 54.1  $\pm$  3.4 kJ mol<sup>-1</sup>. From this value the synergistic influence  $H_{\text{Syn}}$  of an amino and a cyano substituent (capto-dative effect) was calculated by use of eq. 7 with the aid of the RSEs for an amino-alkyl (10a) and for a cyano-alkyl (10b) radical. These RSEs were determined previously in our group [RSE(10a)<sup>[26]</sup> = 4-8 kJ mol<sup>-1</sup>, RSE(10b)<sup>[27]</sup> = 22.2 kJ mol<sup>-1</sup>].

Table 4. Standard enthalpies of formation  $\Delta H_{\rm f}^0(4)$  for the different states (liquid, crystalline, gaseous), enthalpies of vaporization  $\Delta H_{\rm V}$ and enthalpies of fusion  $\Delta H_{\rm m}$  (in kJ mol<sup>-1</sup>)

	State	$\Delta H_{c}$	$\Delta H_{\rm f}^{\circ}(\rm c)$	$\Delta H_{v}$	$\Delta H_{\rm m} ({\rm m.p.})^{[a]}$	$\Delta H_{\rm f}^{\circ}({\rm g})$	$\Delta \Delta H^{[b]}$	Increment
4a	liquid	-2786.38 ± 0.41	69.0 ± 0.5	45.40 ± 0.59		114.39 ± 0.75	-21.8	CH <sub>2</sub> [N,CN]
4b	liquid	-4092.15 ± 0.85	16.1 ± 1.0	49.93 ± 0.27	1	66.0 ± 1.04	-20.2	CH <sub>2</sub> [N,CN]
4c	cryst.	-4478.9 ± 1.0	9.4 ± 1.1	56.02 ± 0.49	17.57 ± 0.21 (20)	83.0 ± 1.2	-22.9	CH <sub>2</sub> [N,CN]
4e	liquid	1	/	50.82 ± 0.33	1	1	1	
4f	liquid	1	1	57.55 ± 0.31	1	1	1	
4g	liquid	1	-61.9 ± 0.9 <sup>[22]</sup>	57.40 ± 0.38	1	-4.5 ± 1.0	-5.7	CH[N,CN,C]
4i	liquid	1	. /	56.3 ± 1.1	1	1	1	
4j	cryst.	-5771.92 ± 0.68	-56.30 ± 0.69	57.57 ± 0.44	21.59 ± 0.21 (43)	24.03 ± 0.82	2.8	C[N,CN,C <sub>2</sub> ]
-				80.33 ± 0.45 <sup>[c]</sup>				
4	cryst.	-7496.18 ± 0.37	-84.23 ± 0.44	87.76 ± 0.63 <sup>[c]</sup>	25.44 ± 0.21 (66)	3.53 ± 0.77	2.2	C[N,CN,C <sub>2</sub> ]
41	liquid	-5807.60 ± 0.56	157.53 ± 0.68	62.79 ± 0.43	1	220.32 ± 0.81	-8.0	CH[N,CN,Ph]
4	cryst.	-9679.51 ± 0.82	-46.59 ± 0.89	111.27 ± 0.70 <sup>[c]</sup>	24.39 ± 0.21 (54)	64.7 ± 1.1	-8.5	CH[N,CN,Ph]
4	cryst.	-7499.5 ± 1.2	97.2 ± 1.7	73.21 ± 0.42	19.71 ± 0.21 (62)	190.1 ± 1.8	-7.9	CH[N,CN,Ph]

<sup>[a]</sup> Melting point in °C. - <sup>[b]</sup> Eq. 3. - <sup>[c]</sup> Enthalpy of sublimation.

$$H_{\text{Syn}} = \text{RSE}(1a) - [\text{RSE}(10a) + \text{RSE}(10b)]$$
(7)

In contrast to the theoretical investigations<sup>[11,12]</sup> (see introduction) we found a synergistic interaction between the amino and the cyano group of  $H_{Syn} = 26 \text{ kJ mol}^{-1}$ . This value is slightly smaller than the synergistic effect for an amino-ethoxycarbonyl-substitution<sup>[9,10]</sup> (28.5 kJ mol<sup>-1</sup>), but markedly smaller than for an amino-carbonyl-substitution<sup>[8]</sup> (40.6 kJ mol<sup>-1</sup>). This is an indication that the synergistic effect is caused by the resonance between the two substituents. The carbonyl group, which is the strongest electrophilic group of the three substituents shows the strongest synergistic interaction. The ethoxycarbonyl and the cyano group are similar in their ability for homoconjugation (see above) and, accordingly, show a similar synergistic effect. In order to investigate the resonance effect of the substituents at the radical center we correlate the  $H_{\alpha}$ coupling constants of the ESR spectra with the RSE values of the radicals. This will be the topic of a future publication<sup>[28]</sup>.

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### **Experimental Section**

<sup>1</sup>H NMR: WM 250, Bruker. – <sup>13</sup>C NMR: AM 400, Bruker. – MS: Mat44s, Finnigan. – EA: Analyser 240, Perkin-Elmer. – GC: Vega Series 6000, Carlo Erba, Hewlett Packard Integrator 3390A. – DSC: DSC-2, Perkin-Elmer. – Melting points: Büchi apparatus, uncorrected. – Thermolysis: Lauda constant-temperatur bath NB-315 (oil-filled). The activation parameters were calculated by weighted linear correlations<sup>[29]</sup> and the standard deviation of the mean is given.

meso-2,3-Bis(dimethylamino)succinodinitrile (meso-3a): To a solution of 10.32 g (126.6 mmol) of dimethylamine hydrochloride and 5.85 g (89.9 mmol) of potassium cyanide in 30 ml of water, 5.0 ml of a solution of glyoxal (8.8 M) in water was slowly added dropwise. After 2 d, a white precipitate had formed which was separated from the brown solution by filtration and recrystallized from dimethoxyethane. Yield 0.86 g (12%). – M.p. 172–173°C. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 2.44$  (s, 12H, NCH<sub>3</sub>), 3.82 (s, 2H, NCHCN). – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 42.32$  (NCH<sub>3</sub>), 60.13 (NCHCN), 113.32 (CN). – C<sub>8</sub>H<sub>14</sub>N<sub>4</sub> (166.2): calcd. C 57.81, H 8.43, N 33.70; found C 57.83, H 8.43, N 33.70. – An X-ray analysis of the crystals showed that the precipitate had the *meso* configuration<sup>[13]</sup>; the DL isomer could not be isolated from the mother liquor.

*meso- and DL-2,3-Bis(dimethylamino)succinodinitrile (meso-* and DL-**3a**): A solution of 11.54 g (137.2 mmol) of dimethylaminoacetonitrile and 2.03 g (13.9 mmol) of di-*tert*-butyl peroxide in 60 ml of benzene (p.a. quality) was irradiated for 18 h with a 125-W mercury lamp. During irradiation the solution was flushed with nitrogen and cooled with water. The solvent and the monomer were removed and the precipitate was triturated with methanol. Yield 230 mg (14%). - <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.40 (s, DL-NCH<sub>3</sub>), 2.44 (s, *meso*-NCH<sub>3</sub>), 3.82 (s, *meso*-NCHCN), 3.88 (s, DL-NCHCN), isolated ratio of *meso* to DL: 7:1.

*2-Methyl-2-phenylpropionyl Chloride* was prepared according to literature precedures<sup>[30]</sup>. – Yield 91%. – B.p. 101–103 °C (10

Torr).  $- {}^{1}$ H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 1.70$  (s, 6H, CH<sub>3</sub>), 7.28–7.44 (m, 5H, ar. H).

2-Methyl-2-phenylpropanol: A solution of 26.12 g (143.0 mmol) of 2-methyl-2-phenylpropionyl chloride in 240 ml of ether was added dropwise to a suspension of 7.8 g (205 mmol) of LiAlH<sub>4</sub> in 160 ml of dry ether and the mixture was refluxed for 1 h. It was hydrolyzed and extracted with ether. The ether was evaporated from the extract and the residual oil was distilled. Yield 16.74 g (78%). – B.p. 72 °C (0.4 Torr). – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 1.35$  (s, 6H, CH<sub>3</sub>), 3.61 (s, 2H, CH<sub>2</sub>), 7.18–7.28 (m, 1H, *p*-ar. H), 7.30–7.42 (m, 4H, *o*-, *m*-ar. H).

2-Methyl-2-phenylpropanal (**6a**): 9.79 g (65.2 mmol) of 2-methyl-2-phenylpropanol was added in one portion to a stirred suspension of 21.18 g (98.72 mmol) of pyridinium chlorochromate in 20 ml of dry dichloromethane. After 2 h 140 ml of dry ether was added and the suspension was extracted. The extraction was repeated with additional two portions (30 ml) of ether. The extracts were filtered over Florisil and the solvent was evaporated. The residual oil was distilled. Yield 6.7 g (85%). – B.p.  $87-90^{\circ}$ C (10 Torr). – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.84 (s, 6 H, CH<sub>3</sub>), 7.26–7.44 (m, 5H, ar. H), 9.51 (s, 1 H, CHO). – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 22.52 (CH<sub>3</sub>), 31.71 (CH<sub>3</sub>), 72.71 (CCHO), 124.41 (C-3), 126.73 (C-2), 128.25 (C-4), 128.90 (C-1), 202.40 (CHO).

2-Dimethylamino-3-methyl-3-phenylbutyronitrile (2a): 2.50 g (16.9 mmol) of 2-methyl-2-phenylpropionaldehyde **6a** was added to a solution of 3.20 g (16.8 mmol) of sodium hydrogen sulfite in 8 ml of water and a white precipitate formed. Then 4.0 ml of an aqueous solution of dimethylamine (40%) was added and after 45 min a solution of 0.82 g (16.7 mmol) of sodium cyanide in 5 ml of water and was added at 0 °C. The mixture was stirred for 4 d. Then it was extracted with ether, the extract was dried with sodium sulfate and distilled. Yield 0.7 g (20%). – B.p. 117–120 °C (10 Torr). – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.51 (s, 3H, CH<sub>3</sub>), 1.53 (s, 3H, CH<sub>3</sub>), 2.10 (s, 6H, NCH<sub>3</sub>), 3.50 (s, 1H, NCHCN), 7.20–7.40 (m, 3H, *m*-, *p*-ar. H), 7.42–7.50 (m, 2H, *o*-ar. H). – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 26.20 (CH<sub>3</sub>), 26.61 (CH<sub>3</sub>), 41.94 (C<sub>qual</sub>), 44.90 (NCH<sub>3</sub>), 69.86 (NCHCN), 115.77 (CN), 126.80 (C-3), 126.92 (C-2), 128.32 (C-4), 144.25 (C-1).

2,2-Diphenylpropionyl Chloride: 25.38 g (112.2 mmol) of 2,2-diphenylpropionic acid, 19.98 g (168.0 mmol) of thionyl chloride and 1 ml of dimethylformamide were stirred for 1 h at room temp. and then refluxed for 1 h. By distillation 26.5 g (97%) of the acid chloride was isolated. – B.p. 127–130 °C (0.5 Torr). – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 2.10$  (s, 3 H, CH<sub>3</sub>), 7.20–7.30 (m, 4 H, *o*-ar. H), 7.30–7.44 (m, 6 H, *m*-, *p*-ar. H).

2.2-Diphenylpropanol: 16.0 g (65.5 mmol) of 2,2-diphenylpropionyl chloride in 50 ml of dry ether was added dropwise to a suspension of 3.60 g (94.8 mmol) of LiAlH<sub>4</sub> in 100 ml of dry ether. The mixture was stirred for 48 h and then refluxed for 2 h. Then 40 ml of water was added. The precipitate was filtered, the solution was extracted with ether and the extract dried with sodium sulfate. The solvent was removed and the residue was distilled. Yield 10.4 g (75%). – B.p. 136 °C (0.7 Torr). – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 1.32$  (t, 1 H, J = 7 Hz, OH), 1.83 (s, 3 H, CH<sub>3</sub>), 4.13 (d, J = 7 Hz, 2 H, CH<sub>2</sub>), 7.20–7.38 (m, 10 H, ar. H).

2,2-Diphenylpropionaldehyde (**6b**): 8.88 g (41.4 mmol) of pyridinium chlorochromate was added to a stirred solution of 5.59 g (26.0 mmol) of 2,2-diphenylpropanol in 20 ml of dry dichloromethane. After 4 h the mixture was extracted with ether and the extract was filtered through silica gel. The solvent was removed and the residual oil was distilled. Yield 5.38 g (98%). – B.p. 105 °C (0.5 Torr).

## FULL PAPER

- <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 1.80$  (s, 3 H, CH<sub>3</sub>), 7.15–7.22 (m, 4H, *o*-ar. H), 7.28–7.45 (m, 6H, *m*-, *p*-ar. H), 9.92 (s, 1H, CHO).

2-Dimethylamino-3,3-diphenylbutyronitrile (2b): 3.40 g (16.2 mmol) of 2,2-diphenylpropionaldehyde 6b was added to a solution of 3.00 g (15.8 mmol) of sodium hydrogen sulfite and a white precipitate appeared. After 15 min an aqueous solution of dimethylamine (7.9 M, 4.4 ml) was added dropwise. After additional 20 min 1.60 g (32.7 mmol) of sodium cyanide was added and the mixture was stirred for 24 h. It was extracted with ether, the extract was dried with sodium sulfate and the solvent was removed. The residue was chromatographed on silica gel with a mixture of cyclohexane and ethyl acetate (2:1) as eluent. The product was recrystallized from ethanol. Yield 0.65 g (22%). - M.p. 92–93°C. - <sup>1</sup>H NMR  $(250 \text{ MHz}, \text{CDCl}_3): \delta = 1.83 \text{ (s, 3H, CH}_3), 2.10 \text{ (s, 6H, N(CH}_3)_2),$ 4.28 (s, 1 H, NCHCN), 7.15-7.40 (m, 10 H, ar. H). - <sup>13</sup>C NMR  $(100 \text{ MHz}, \text{ CDCl}_3)$ :  $\delta = 27.88 (\text{CH}_3), 44.94 [N(\text{CH}_3)_2], 50.84$ (CCH<sub>3</sub>), 66.95 (NCHCN), 115.71 (CN), 127.11, 127.62, 128.13,  $128.24, 128.78, 144.18, 146.41. - C_{18}H_{20}N_2$  (264.4): calcd. C 81.77, H 7.62, N 10.59; found C 81.51, H 7.48, N 10.43. - As by-product 2,2-diphenylpropionaldehyde cyanohydrin was isolated: Yield 1.76 g (49%). – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 1.89$  (s, 3 H, CH<sub>3</sub>), 2.4 (br., 1 H, OH), 5.14 (s, 1 H, OCHCN), 7.25–7.40 (m, 10 H, ar. H).

Dimethylaminoacetonitrile (4a): Commercially available.

Diethylaminoacetonitrile (4b): Commercially available.

2-Piperidinoacetonitrile (4c): Yield 47% (ref.<sup>[14]</sup> 94%). – B.p. 90°C (10 Torr), [ref.<sup>[14]</sup> 83°C (9 Torr)]. – M.p. 20°C (ref.<sup>[14]</sup> 20°C). – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 1.40$  (m, 2H, CH<sub>2</sub>), 1.58–1.70 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 2.50–2.58 (m, 4H, NCH<sub>2</sub>), 3.50 (s, 2H, NCH<sub>2</sub>CN). – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 23.08$  (CH<sub>2</sub>), 25.45 (NCH<sub>2</sub>CH<sub>2</sub>), 46.63 (NCH<sub>2</sub>), 52.86 (NCH<sub>2</sub>CN), 120.37 (CN).

2-Dimethylaminopropionitrile (4d): Yield 38% (ref.<sup>[14]</sup> 28%). – B.p. 49 °C (40 Torr) [ref.<sup>[14]</sup> 59–61 °C (40 Torr)]. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.47 (d, *J* = 7 Hz, 3 H, CH<sub>3</sub>), 2.35 (s, 6 H, NCH<sub>3</sub>), 3.65 (q, *J* = 7 Hz, 1 H, NCHCN). – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 17.58 (CH<sub>3</sub>), 41.33 (NCH<sub>3</sub>), 53.01 (NCHCN), 116.95 (CN).

2-Diethylaminopropionitrile (4e): Yield 37% (ref.<sup>[14]</sup> 68%). – B.p. 73–80 °C (54 Torr) [ref.<sup>[14]</sup> 55 °C (11 Torr)]. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.10 (t, *J* = 7 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>), 1.50 (d, *J* = 7 Hz, 3H, CH<sub>3</sub>), 2.46–2.51 (m, 4H, CH<sub>2</sub>), 2.61–2.83 (m, 4H, CH<sub>2</sub>), 3.83 (q, 1H, *J* = 7 Hz, NCHCN).

2-Piperidinopropionitrile (4f): Yield 29%. – B.p. 91°C (16 Torr). – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.44–1.56 (m, 2H, CH<sub>2</sub>), 1.57 (d, *J* = 7 Hz, 3H, CH<sub>3</sub>), 1.57–1.70 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 2.32–2.46 (m, 2H, NCH<sub>2</sub>), 2.58–2.70 (m, 2H, NCH<sub>2</sub>), 3.65 (q, *J* = 7 Hz, 4H, NCHCN). – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 17.23 (CH<sub>3</sub>), 24.07 (CH<sub>2</sub>), 25.77 (NCH<sub>2</sub>CH<sub>2</sub>), 50.72 (NCH<sub>2</sub>), 53.08 (NCH<sub>2</sub>CN), 117.68 (CN).

2-Diethylaminopentanenitrile (4g): Yield 88% (ref.<sup>[14]</sup> 44%). – B.p. 84–89 °C (22 Torr) [ref.<sup>[14]</sup>: 95 °C (15 Torr)]. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.97 (t, *J* = 8 Hz, 3 H, CH<sub>3</sub>), 1.10 (t, *J* = 8 Hz, 6 H, NCH<sub>2</sub>CH<sub>3</sub>), 1.40–1.58 (m, 2 H, CH<sub>2</sub>), 1.64–1.80 (m, 2 H, CH<sub>2</sub>), 2.35–2.48 (m, 2 H, NCH<sub>2</sub>), 2.63–2.80 (m, 2 H, NCH<sub>2</sub>), 3.63 (t, *J* = 8 Hz, 1 H, NCHCN). – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 13.36 (NCH<sub>2</sub>CH<sub>3</sub>), 13.45 (CH<sub>3</sub>), 19.92 (CH<sub>2</sub>CH<sub>3</sub>), 34.00 (CH<sub>2</sub>), 45.28 (NCH<sub>2</sub>), 53.85 (NCHCN), 118.63 (CN).

2-Dimethylamino-2-methylpropionitrile (**4h**): Yield 76% (ref.<sup>[14]</sup>) 52–69%). – B.p. 56–58°C (27 Torr) [ref.<sup>[14]</sup>: 57°C (25 Torr)]. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.52 (s, 6H, CH<sub>3</sub>), 2.36 (s, 6H, NCH<sub>3</sub>).  $-^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 26.77$  (CH<sub>3</sub>), 40.72 [N(CH<sub>3</sub>)<sub>2</sub>], 53.15 (CCN), 119.62 (CN).

2-Diethylamino-2-methylpropionitrile (4i): Yield 31% (ref.<sup>[14]</sup> 30-39%). – B.p. 70-75°C (24 Torr) [ref.<sup>[14]</sup> 72-74°C (14 Torr)]. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.13 (t, *J* = 7 Hz, 6H, NCH<sub>2</sub>CH<sub>3</sub>), 1.52 (s, 6H, CH<sub>3</sub>), 2.75 (q, *J* = 7 Hz, 4H, NCH<sub>2</sub>CH<sub>3</sub>).

2-*Methyl-2-piperidinopropionitrile* (**4j**): Yield 65%. – M.p. 43 °C. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.40–1.57 (m, 2H, CH<sub>2</sub>), 1.53 (s, 6H, CH<sub>3</sub>), 1.58–1.70 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 2.54–2.66 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>). – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 23.99 (CH<sub>2</sub>), 26.18 (NCH<sub>2</sub>CH<sub>2</sub>), 26.47 (CH<sub>3</sub>), 48.59 (NCH<sub>2</sub>), 56.43 (CCN), 120.37 (CN).

*1-Cyano-1-piperidinocyclohexane* (**4k**): Yield 92%. – M.p. 66°C. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.20–1.33 (m, 1H, CH), 1.43–1.67 (m, 11H, CH<sub>2</sub>), 1.73–1.84 (m, 2H, CH<sub>2</sub>), 2.08–2.20 (m, 2H, CH<sub>2</sub>), 2.55–2.64 (m, 4H, NCH<sub>2</sub>). – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 22.31 (CH<sub>2</sub>), 24.41 (CH<sub>2</sub>), 25.08 (CH<sub>2</sub>), 26.34 (CH<sub>2</sub>), 34.16 [N(CN)CCH<sub>2</sub>], 47.63 (NCH<sub>2</sub>), 61.52 (NCCN), 119.54 (CN).

2-Dimethylamino-2-phenylacetonitrile (41): Yield 69% (ref.<sup>[14]</sup> 29%). – B.p. 71–73°C (0.6 Torr) [ref.<sup>[14]</sup> 90°C (6 Torr)]. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.32 (s, 6H, NCH<sub>3</sub>), 4.87 (s, 1H, NCHCN), 7.30–7.45 (m, 3H, *m*-, *p*-ar. H), 7.48–7.56 (m, 2H, *o*-ar. H). – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 41.69 (NCH<sub>3</sub>), 63.07 (NCHCN), 114.99 (CN), 127.77 (C-3), 128.72 (C-2), 128.85 (C-4), 133.71 (C-1).

2-(4-tert-Butylphenyl)-2-(diethylamino)acetonitrile (4m): M.p. 54°C.  $^{-1}$ H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 1.10$  (t, J = 8 Hz, 6H, CH<sub>3</sub>), 1.35 [s, 9H, C(CH<sub>3</sub>)<sub>3</sub>], 2.40–2.54 (m, J = 8 Hz, 2H, NCH<sub>2</sub>), 2.63–2.78 (m, J = 8 Hz, 2H, NCH<sub>2</sub>), 5.00 (s, 1 H, CH), 7.38–7.50 (m, 4H, ar. H).  $^{-13}$ C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 13.25$  [C(CH<sub>3</sub>)<sub>3</sub>], 31.38 (NCH<sub>2</sub>CH<sub>3</sub>), 34.68 [C(CH<sub>3</sub>)<sub>3</sub>], 44.95 (NCH<sub>2</sub>), 58.03 (NCHCN), 116.67 (CN), 125.69 (C-3), 127.41 (C-2), 131.61 (C-4), 151.73 (C-1).

2-Phenyl-2-piperidinoacetonitrile (**4n**): Yield 42%. – M.p. 62°C. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.43–1.52 (m, 2H, CH<sub>2</sub>), 1.52–1.68 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 2.44–2.56 (m, 4H, NCH<sub>2</sub>), 4.80 (s, 1H, NCHCN), 7.31–7.40 (m, 3H, *m*-, *p*-ar. H), 7.50–7.56 (m, 2H, *o*-ar. H). – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 23.97 (CH<sub>2</sub>), 25.83 (NCH<sub>2</sub>CH<sub>2</sub>), 50.93 (NCH<sub>2</sub>), 63.03 (NCHCN), 115.61 (CN), 127.84 (C-3), 128.66 (C-2), 128.69 (C-4), 133.65 (C-1).

*cis- and trans-2,3-Bis(dimethylamino)acrylonitrile* (7) were prepared according to literature procedures<sup>[31,32,33,34]</sup>: Yield 22%. – B.p. 109–110°C (10 Torr) [ref.<sup>[34]</sup> 109–110°C (10 Torr)]. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.44 [s, 6H, *cis-*, *trans-*N(CH<sub>3</sub>)<sub>2</sub>], 3.01 [s, 6H, *trans-*N(CH<sub>3</sub>)<sub>2</sub>], 3.07 [s, 6H, *cis-*N(CH<sub>3</sub>)<sub>2</sub>], 5.97 (s, 1H, *cis-*CH), 6.74 (s, 1H, *trans-*CH).

#### **Kinetic Measurements**

Isomerization of 3a: 0.1-ml samples of a solution of pure meso-3a in [D<sub>6</sub>]benzene (60 mM) were degassed and sealed under N<sub>2</sub> into small glass ampoules of about 0.3 ml. These ampoules were heated for a definite time at a constant temperature in an oil bath (±0.2 °C). After cooling to room temp, the content of each ampoule was placed in an NMR tube and diluted with [D<sub>6</sub>]benzene. Integration of the signals of the *N*-methyl protons (see Table 6) in the <sup>1</sup>H-NMR spectra (250 MHz) gave the relative ratio of meso- to DL-3a. Four substances could be detected in the NMR spectra: mesoand DL-3a and a mixture of *cis*- and *trans*-2-dimethylaminomaleic nitrile 7, which was formed by HCN elimination from meso-3a and DL-3a. All substances were clearly indentified by independent synthesis and the <sup>1</sup>H-NMR spectra of the reference compounds showed the same chemical shifts as the substances observed during the isomerization. Table 6 contains the chemical shifts of the signals, which were used for the determination the relative concentrations.

Table 6. <sup>1</sup>H-NMR shifts<sup>[a]</sup> of signals of *meso-* and DL-**3a** and of *cis-* and *trans-7* in [D<sub>6</sub>]benzene

meso-3a	N(CH <sub>3</sub> ) <sub>2</sub>	1.38	cis-7	N(CH <sub>3</sub> ) <sub>2</sub>	2.28
	СН	3.27		N(CH <sub>3</sub> ) <sub>2</sub>	2.28
				СН	5.40
DL-3a	N(CH <sub>3</sub> ) <sub>2</sub>	1.80	trans-7	N(CH <sub>3</sub> ) <sub>2</sub>	2.20
	СН	3.08		N(CH <sub>3</sub> ) <sub>2</sub>	2.45
				СН	6.38

[a] In ppm vs. TMS.

For the evaluation of the isomerization kinetics a slightly changed equation from ref.<sup>[15]</sup> was used (eq. 1). Since the formation of 7 by elimination of HCN from dimer 3a lowers its concentration,  $c_0$  of meso-3a was taken as the sum of the concentrations of meso-**3a** and DL-**3a** ( $c_0 = c_{meso} + c_{DL}$ ). The concentrations of meso-**3a** and DL-3a ( $c_{meso}$  and  $c_{DL}$ ) were determined from the N-methyl signals of the <sup>1</sup>H-NMR spectra. The equilibrium constant K at each temperature was available from the equilibrium concentration of meso-3a and DL-3a after more than eight half-life periods. The correlation of  $\ln\{(Kc_{meso} - c_{DL})/Kc_0\}$  versus time was linear, from which the sum of the rate constants  $(k_1 + k_2)$  was obtained. With the equilibrium constant K at the respective temperature the constants  $k_1$  and/or  $k_2$  of the homolytic bond cleavage were available. The results of the isomerization kinetics between meso- and DL-3a are shown in Table 7. From the plot of  $\ln k_1$  (or  $\ln k_2$ , respectively) versus the reciprocal temperature the activation parameters of the homolytic bond cleavage of meso-3a and DL-3a were obtained.

Table 7. Rate constants of the homolytic bond cleavage of the dimer **3a** measured by the isomerization of *meso-***3a** in an equilibrium mixture of *meso-* and DL-**3a** in [D<sub>6</sub>]benzene by <sup>1</sup>H NMR

T	k1+k2	Error	n <sup>[a]</sup>	к	k1	<b>K</b> 2
[°C]	[s <sup>-1</sup> ]	[%]			[s <sup>-1</sup> ]	[s <sup>-1</sup> ]
180	$1.59 \times 10^{-4}$	3.9	6	0.28	3.48 × 10 <sup>-5</sup>	$1.24 \times 10^{-4}$
190	3.63 × 10 <sup>-4</sup>	2.3	6	0.33	9.00 × 10 <sup>-5</sup>	2.73 × 10 <sup>-4</sup>
200	9.65 × 10 <sup>-4</sup>	3.8	6	0.36	2.55 × 10 <sup>-4</sup>	7.10 × 10 <sup>-4</sup>
216	3.40 × 10 <sup>-3</sup>	1.3	5	0.41	9.89 × 10 <sup>-4</sup>	2.41 × 10 <sup>-3</sup>
224	1	1	1	0.44	1	1

<sup>[a]</sup> Number of NMR samples.

Table 8. Rate constants of the homolytic bond cleavage from kinetic measurements of the concentration of **2a** and **2b** with thiocresol as radical scavenger

	Т	<i>k</i> <sub>1</sub>	Error	n <sup>[a]</sup>	Interval <sup>[b]</sup>
	[°C]	[s <sup>-1</sup> ]	[%]		
2a	210.0	1.00 × 10 <sup>-4</sup>	2.7	9	3.6
	219.5	1.76 × 10 <sup>-4</sup>	1.8	7	3.6
	228.5	3.27 × 10 <sup>-4</sup>	2.6	12	4.2
	238.5	6.18 × 10 <sup>-4</sup>	1.4	9	3.7
	248.0	1.03 × 10 <sup>-3</sup>	3.0	7	2.2
2b	170.5	7.70 × 10 <sup>-5</sup>	3.5	12	1.7
	180.0	1.91 × 10 <sup>-4</sup>	3.3	9	3.6
	190.0	5.49 × 10 <sup>-4</sup>	8.0	13	4.6
	201.0	1.03 × 10 <sup>-3</sup>	3.7	10	3.6
	210.0	2.83 × 10 <sup>-3</sup>	3.9	8	4.4

<sup>[a]</sup> Number of ampoules for each rate constant. - <sup>[b]</sup> Observed half-life times.

Table 9. Vapor pressure of 4 determined by the method of trans-<br/>ference

	T <sup>[a]</sup>	m <sup>[b]</sup>	N2 <sup>[C]</sup>	[d]	1	T <sup>[a]</sup>	m <sup>[b]</sup>	N <sub>2</sub> <sup>[c]</sup>	p <sup>[d]</sup>
40	4.4	7.02	0.841	2 503	<b>4</b> i	50.1	5.90	0 760	1 27
-70	94	6 17	0.513	3 589	1	55.0	7 02	0.640	1 79
	144	7 41	0.421	5 2 3 2		60.2	7 79	0.510	2.49
	19.4	9.89	0.412	7.112		65.2	8.49	0.420	3.29
	24.4	13.4	0.421	9.411		70.2	10.0	0.360	4,54
	29.5	10.9	0 252	12 78		75.1	12.1	0.330	6.00
	34.5	14.3	0.240	17.55	{	80.3	10.3	0.210	7.97
4b	10.2	2 70	0.888	0.768	4i <sup>[e]</sup>	15.0	5.72	21.680	4.31 × 10 <sup>-2</sup>
	15.2	2.24	0.499	1.087	· ·	20.1	4.06	8.900	7.44 × 10 <sup>-2</sup>
	20.2	2 46	0.365	1.578		25.2	7.84	9,610	1.33 × 10 <sup>-1</sup>
	25.2	2.71	0.280	2,217		30.2	9.05	6.370	$2.32 \times 10^{-1}$
	30.0	3.34	0.244	3.111		35.3	7.69	3.240	3.87 × 10 <sup>-1</sup>
	35.1	3.49	0.183	4,295		38.2	6.29	1.980	5.17 × 10 <sup>-1</sup>
	40.1	4.06	0.158	5,760		41.3	7.93	1.840	$7.03 \times 10^{-1}$
	45.1	3.82	0 110	7.756	4k <sup>[e]</sup>	15.2	$7.05 \times 10^{-2}$	132.800	5.39 × 10 <sup>-5</sup>
4c	29.5	9.27	0.432	0.431		20.3	$8.14 \times 10^{-2}$	70.900	1.16 × 10 <sup>-4</sup>
	35.0	15.0	4.510	0.666		23.2	$9.50 \times 10^{-2}$	49.700	$1.94 \times 10^{-4}$
	39.9	8.60	1.860	0.926		26.3	$1.06 \times 10^{-1}$	35.570	$3.02 \times 10^{-4}$
	45.1	8.24	1.240	1.329		29.2	$4.45 \times 10^{-1}$	95.050	4.75 × 10 <sup>-4</sup>
	50.0	7.83	0.849	1.843		34.1	$5.07 \times 10^{-1}$	52.930	$9.72 \times 10^{-4}$
	54.9	7.03	0.584	2.407		40.1	8.09 × 10 <sup>-1</sup>	37.040	$2.21 \times 10^{-3}$
	60.0	6.96	0.416	3.341	-	45.2	1.04	24.840	4.27 × 10 <sup>-3</sup>
	64.9	6.10	0.266	4.584	ļ	48.2	9.33 × 10 <sup>-1</sup>	15.370	$6.16 \times 10^{-3}$
4e	5.6	5.56	2.306	0.495		52.1	1.52	14.250	$1.08 \times 10^{-2}$
	10.2	5.04	1.421	0.718	41	25.1	6.01	24.720	3.77 × 10 <sup>-2</sup>
	15.2	5.17	0.980	1.058		30.2	6.01	15.630	5.97 × 10 <sup>-2</sup>
	20.2	6.04	0.790	1.523	1	35.1	6.93	11.930	9.01 × 10 <sup>-2</sup>
	25.1	6.56	0.600	2.169		40.2	5.47	6.290	1.35 × 10 <sup>-1</sup>
	30.0	7.22	0.474	3.013		45.1	5.26	4.200	1.94 × 10 <sup>-1</sup>
	35.1	6.61	0.316	4.135		50.1	4.35	2.440	2.76 × 10 <sup>-1</sup>
	40.1	4.52	0.157	5.676		55.1	3.39	1.302	4.03 × 10 <sup>-1</sup>
	45.2	3.64	0.095	7.550	1	60.1	3.54	0.987	5.55 × 10 <sup>-1</sup>
4f	10.2	1.47	3.260	$8.22 \times 10^{-2}$		65.1	3.85	0.783	7.61 × 10 <sup>-1</sup>
	15.1	1.76	2.490	1.28 × 10 <sup>-</sup>	4m <sup>ie)</sup>	30.1	2.06	64.230	4.13 × 10 <sup>-3</sup>
	20.2	2.00	1.870	1.93 × 10 <sup>-1</sup>		35.1	2.39	41.800	7.37 × 10 <sup>-3</sup>
	25.3	2.19	1.340	2.94 × 10 <sup>-</sup>	]	40.4	3.44	32.600	1.36 × 10 <sup>-2</sup>
	30.3	2.29	0.970	4.26 × 10 <sup>-</sup>	[	45.2	4.55	25.700	2.28 × 10 <sup>-2</sup>
	35.3	2.45	0.710	6.19 × 10		50.1	4.11	14.700	3.61 × 10 <sup>-*</sup>
	40.3	2.46	0.510	8.64 × 10 <sup>-</sup>		55.3	8.56	18.400	6.00 × 10 <sup>-2</sup>
	45.2	2.60	0.380	1.227		60.1	5.40	7.270	$9.57 \times 10^{-2}$
4g	10.3	1.85	2.740	1.08 × 10		63.3	4.88	4.740	$1.33 \times 10^{-2}$
	15.1	2.17	2.090	1.67 × 10	4n	65.1	1.93	4.568	5.34 × 10 <sup>-2</sup>
	20.2	2.45	1.570	2.51 × 10		70.1	1.25	2.000	7.83 × 10 °
	25.1	2.68	1.120	3.84 × 10 '		75.1	1.45	1.584	1.14 × 10
	30.3	2.80	0.816	$5.51 \times 10^{-1}$		80.1	1.48	1.140	$1.62 \times 10^{-1}$
	35.2	2.98	0.601	7.92 × 10		85.1	1.36	0.744	2.28 × 10 <sup>-1</sup>
	40.1	3.03	0.431	1.130	1	90.1	1.51	0.600	3.12 × 10
	45.0	3.11	0.323	1.04/ 1.00 - 10 <sup>-1</sup>		90.1 100	1./9	0.304	4.42 × 10 5.04 ··· 40 <sup>-1</sup>
41	5.5	2.07	2.5/3	1.69 × 10 2.04 ·· 10 <sup>-1</sup>	ł	100.	1.72	0.300	0.94 × 10 7.02 × 10 <sup>-1</sup>
	10.2	2.00	1.009	3.04 × 10 4.62 ·· 10 <sup>-1</sup>	{	103.	1.55	0.240	7.93 × 10
	10.1	2.02	1.093	4.02 × 10 6.52 × 10 <sup>-1</sup>					
	20.0	3.23	0.670	$0.03 \times 10^{-1}$	}				
	20.0	3.14	0.070	5.94 × 10 1.44 ∪ 10 <sup>-1</sup>					
	25.0	ч.∠о 3.86	0.329	$1.94 \times 10^{-1}$					

<sup>[a]</sup> Temperature in °C. - <sup>[b]</sup> Transported substance in mg. - <sup>[c]</sup> Nitrogen volume in I. - <sup>[d]</sup> Vapor pressure in Torr. - <sup>[e]</sup> Sublimation.

Table 10. Enthalpies of combustion  $\Delta u_c$  of **4** and their mean values  $(Jg^{-1})$ 

	4a	4b	4c	4j
$\Delta u_{\rm C}(4)$	-33091.3	-36420.7	-36058.3	-37864.5
	-33109.7	-36415.2	-36023.2	-37869.2
	-33092.9	-36454.9	-36009.6	-37871.3
	-33087.5	-36443.7	-36020.5	-37851.5
		-36443.4	-36018.8	
mean value	$-33095.4 \pm 8.5$	-36435.6 ± 15.1	-36026.1 ± 16.7	-37864.1 ± 7.7
	4k	41	4m	4n
$\Delta u_{\rm C}(4)$	-38922.7	-36219.6	-39560.1	-37431.5
	-38929.3	-36218.6	-39550.5	-37388.8
	-38934.7	-36203.0	-39561.0	-37407.9
	-38928.8	-36218.8		-37407.0
	-38928.6	-36222.9		-37398.9
mean value	$-38928.8 \pm 3.8$	$-36216.6 \pm 7.0$	-39557.2 ± 4.8	-37406.8 ± 14.1

Table 11. Heat capacities  $c_p^{298}$  determined by DSC, densities  $d^{298}$  and expansion coefficients (dV/dT) of 4

<u></u>	T		Polynomial <sup>[a]</sup>		C, <sup>298</sup>	c. <sup>298</sup>	d <sup>298</sup>	(dV/d7) <sup>[b]</sup>
	[K]	<i>k</i> <sub>1</sub>	k <sub>2</sub>	с	[cal g <sup>-1</sup> K <sup>-1</sup> ]	[J g <sup>-1</sup> K <sup>-1</sup> ]	[g cm <sup>-1</sup> ]	$[10^{-6}   g^{-1} K^{-1}]$
4a	279-311	0.0000217	-0.0159640	3.2867546	0.45	2.26	0.87	1.0
4b	281-313	0.0000461	-0.0299445	5.2913962	1.94	8.12	0.87	1.0
4c	298-341	0.0000169	-0.0105176	2.3697028	0.74	3.56	0.96	1.0
4d	282-332	0.0000307	-0.0190284	3.5715149	0.63	2.64	1	1.0
4e	280-308	0.0000209	-0.0160501	3.4389055	0.51	2.13	1	1.0
4f	280-330	0.0000139	-0.0105779	2.2796891	1.46	6.11	0.93	1.0
4h	282-332	0.0000372	-0.0228724	4.0560362	0.54	2.26	1	1.0
4i	280-313	0.0000145	-0.0076853	1.4997383	0.50	2.10	1	1.0
4j	277-295	0.0001980	-0.1050175	14.2821561	1.67	6.99	0.95	1.0
4k	278-322	0.0001390	-0.0072348	1.2553792	1.60	6.69	1.04	0.1
41	279-311	0.0000320	-0.0219004	4.0328383	1.46	6.11	0.99	1.0
4m	278-302	0.0000451	-0.0250902	3.8178654	0.35	1.46	1.03	0.1
4n	281-313	0.0000149	-0.0078961	1.3741294	1.42	5.94	1.13	1.0

<sup>[a]</sup>  $c_p$  [cal  $g^{-1}$  K<sup>-1</sup>] =  $k_1 T^2 + k_2 T + c_r$ , from the best fit of the DSC curve. - <sup>[b]</sup> Estimated.

Thermal Decomposition of 2: Solutions of 2a or 2b and thiocresol (concentration 2a 104 mM, thiocresol 1.14 M; concentration 2b 108 mм, thiocresol 1.135 м) in mesitylene were prepared. To these solutions octadecane was added as internal standard. 0.1-ml samples of these solutions were sealed under N2 into small glas ampoules of about 0.3 ml. These ampoules were heated for a definite time in a thermostated oil bath ( $\pm 0.2$ ). The concentration of the first ampoule (after 5 min, at 216 °C after 4 min) was used as zero sample. The concentration  $C_i(t)$  of **2** was measured by GC (internal standard octadecane). The plot of  $\ln(c_0/c_i)$  versus time gives a linear relation from which the rate constant  $k_1$  (at each temperature) was obtained (Table 8). The activation parameters for the homolytic bond cleavage of 2 were obtained from the Eyring equation (Table 1).

DSC Measurements of 2b: 3-4 mg of 2b together with a mixture of thiocresol and solvent (see Table 2) was given into small screwable high-pressure steel pans. The sample and the reference compound were heated in a differential scanning calorimeter at a constant heating rate of 5 °C min<sup>-1</sup> (sensitivity: 1.0 mcal  $s^{-1}$ ). The activation parameters of the thermal decomposition of 2b were obtained by simulation of the signals (Table 2). For details about the method see ref.<sup>[19]</sup>.

#### **Thermochemical Measurements**

Enthalpies of Combustion: For measurement of the enthalpies of combustion an isoperibolic macrocalorimeter<sup>[35]</sup> was used. Because of slight modifications of the calorimeter during the measuring series different heat equivalents for the calorimeter were obtained from calibration measurements with benzoic acid (sample 39i, National Bureau of Standards). The values found were  $\varepsilon = 25066.7$  $\pm$  1.8 J K  $^{-1}$  for 4a,  $\epsilon=25104.5\pm3.1$  J K  $^{-1}$  for 4b, 4n,  $\epsilon=25089.5$  $\pm$  1.2 J K  $^{-1}$  for 4c, 4k, 4l and  $\epsilon$  = 25096.64  $\pm$  0.54 J K  $^{-1}$  for 4f, 4i, 4m). The energy of ignition was determined to be 1.46 J. The substances were pressed into tablets of ca. 300 mg weight or sealed in polyethylene foils. The detailed procedure was described previously<sup>[36]</sup>. For the reduction of the data to standard conditions conventional procedures<sup>[37]</sup> were used. The specific heat capacities were measured by DSC (Table 11).

Enthalpies of Sublimation and Enthalpies of Vaporization: The enthalpies of sublimation and vaporization were determined by the method of transference in a saturated nitrogen stream<sup>[38,39,40]</sup>. 0.2-0.3 g of the substance was mixed with ca. 10 ml of glass beads ( $\emptyset$  0.5 mm) and the mixture was placed into a thermostated Utube. At several different temperatures a nitrogen stream was passed through the U-tube for a definite time. The transported material was collected in a second (cooled) U-tube and its amount was determined by gas chromatography with the method of the internal standard. The enthalpies of vaporization or sublimation were calculated by use of eq. 8 from the vapor pressure p of the substances at each temperature (Table 9).

$$\Delta H_{\rm V} = -\mathbf{R}[d\ln(p)/\mathrm{d}T] \tag{8}$$

- \* Dedicated to Professor Horst Prinzbach on the occasion of his 65th birthday.
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