Preferred Formation of *anti*-Housane (Retention) in the Sensitized Photodenitrogenation of Cyclopentane-Annellated DBH-Type Azoalkanes through Long-Range Steric Effects in the Cyclization of the Triplet Cyclopentane-1,3-diyl Diradicals

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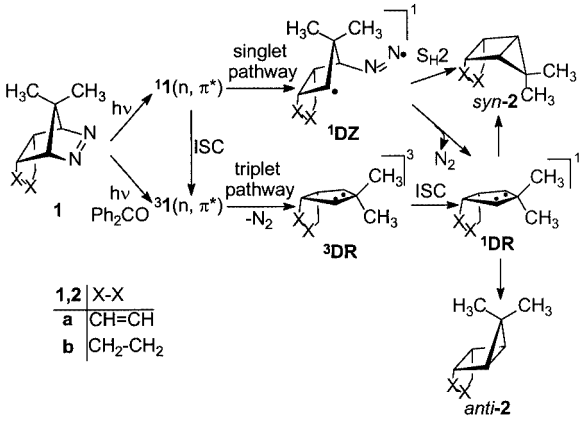
Keywords: DBH / Azoalkanes / Photolysis / Triplet diradical / Long-range steric effects / Diastereoselectivity

The photolysis of the cyclopentene- and cyclopentane-annellated DBH-type azoalkanes **1a** and **1b** affords under singlet conditions (high-temperature direct photolysis) predominantly the inverted housanes *syn*-**2** in similar amounts for both derivatives **2a** and **2b**. Under triplet conditions (low-temperature direct or benzophenone-sensitized photolysis), the photolysis leads to the retained housane *anti*-**2** as the major diastereomer, but with a substantial difference in the *syn*/*anti*-housane ratio for **2a** (38:62) and for **2b** (6:94). This significant difference in the *anti* stereoselectivity of the triplet pathway is mechanistically rationalized in terms of long-range steric interactions between the annellated ring and the *gem*-dimethyl-substituted methylene bridge during the cyclization of the cyclopentane-1,3-diyl triplet diradical ^{3}**DR** after ISC. In contrast, the denitrogenation of the intermediary diazenyl diradical ^{1}**DZ** along the S_H2 pathway (inversion) for the singlet process is quite insensitive to these remote steric effects.

Introduction

Since its discovery in 1967,[1] the preferred formation of inverted housane in the denitrogenation of *exo*-deuterated diazabicyclo[2.2.1]heptene ([D_2]DBH) has been an issue of intensive mechanistic discussion.[2–6] Our recent work on the cyclopentene-annellated DBH derivative **1a** has helped to clarify the complexity of the double inversion process (Scheme 1).[7] We found that in the direct photolysis at elevated temperature (singlet pathway), the inverted housane *syn*-**2a** is produced as the major diastereomer from the intermediary diazenyl diradical ^{1}**DZ** through the S_H2 process.[7] In a competitive pathway, the ^{1}**DR** intermediate is formed by elimination of N_2 from the ^{1}**DZ** species and affords both the inverted (*syn*-**2a**) and retained (*anti*-**2a**) housanes. The product distribution in the direct photolysis is strongly temperature-dependent: While at elevated temperature the *syn*-**2a** housane is slightly favored (*syn*/*anti* ratio 62:38 at +40 °C), the *anti*-**2a** housane dominates slightly at subambient temperature (*syn*/*anti* ratio 39:61 at −75 °C). This observation has been explained by intersystem crossing (ISC) of the n,π*-excited azoalkane, namely ^{1}**1**(n,π*) to ^{3}**1**(n,π*), which competes with the C−N bond cleavage in the singlet pathway. Confirmation of the triplet pathway was achieved by benzophenone-sensitized photolysis which afforded the same *syn*/*anti*-**2a** ratio as in the low-temperature direct photolysis. Thus, at low temperature, ISC is favored over the C−N bond cleavage and the resulting triplet-excited ^{3}**1**(n,π*) azoalkane loses N_2 to produce the planar cyclopentane-1,3-diyl triplet diradical ^{3}**DR**. The latter leads on ISC to a mixture of *syn*/*anti*-**2a** housanes; at high temperature, the S_H2 process prevails to afford the *syn* product through inversion.



Scheme 1

The slight preference of the *anti*-**2a** housane in the triplet pathway has been attributed to a steric interaction between the annellated cyclopentene ring and the *gem*-dimethyl-substituted methylene bridge during the ring closure of the planar nitrogen-free triplet diradical ^{3}**DR**. Indeed, AM1 calculations had confirmed that the *anti*-**2a** diastereomer is by about 6 kcal/mol of lower energy than the more strained

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syn-housane.[8] Thus, only a small fraction (< 0.5 kcal/mol) of this energy bias in favor of the *anti*-**2a** product is utilized in the transition state for cyclization, which is a consequence of the low (< 3 kcal/mol) energy barrier for the ^{3}**DR** → **2a** process. It follows that an increase of the steric interactions of the remote annellated ring and the *gem*-dimethyl-substituted methylene bridge should raise the energy barrier of the ^{3}**DR** → *syn*-**2a** cyclization and, consequently, the formation of *anti*-housane should be enhanced. That this is actually the case, we demonstrate herein for the photodenitrogenation of the saturated azoalkane derivative **1b**. Whereas in the direct photolysis (singlet-excited process), the *syn*/*anti*-**2b** housane ratio is nominally affected by this structural change, for the benzophenone-sensitized photolysis (triplet-excited process) essentially exclusively the *anti*-**2b** housane is observed. This is the first example of such a high extent of retention for the cyclization of a nitrogen-free ^{3}**DR** triplet diradical of the cyclopentane-1,3-diyl type.

Results

The known azoalkanes **1a**,**b** were prepared according to the Hünig route.[9] Upon irradiation with the 351-nm line of an argon-ion laser, their denitrogenation led exclusively to the *syn* and *anti* diastereomers of the housanes **2a**,**b**. The housanes *anti*-**2a** and *syn*-**2a** were obtained as reported,[7] the unknown housanes *anti*-**2b** and *syn*-**2b** were fully characterized by spectroscopic methods in analogy to **2a**. The quantum yield of denitrogenation of the azoalkane **1a** was determined to be Φ_{rel}(**1a**) = 0.84 ± 0.03 relative to **1b** [Φ_{rel}(**1b**) = 1.0], see Exp. Sect. for details.

Although the *syn*/*anti* ratios of the housane **2a** in the denitrogenation of the azoalkane **1a** had been determined before,[7] the photolyses were carried out in parallel with azoalkane **1b** under identical conditions, to enable direct comparison. The *syn*/*anti* product ratios for the direct, triplet-sensitized (benzophenone), and quenched (*trans*-piperylene) photolyses are given in Table 1. The temperature was varied from −75 to +40 °C for the three irradiation modes (for additional data, see Table 2). Control experiments established that no thermal isomerization of the housane *syn*-**2** to the thermodynamically favored *anti*-**2** (AM1 calculation indicates ca. 6 kcal/mol) had taken place even at +40 °C.

Expectedly, for both azoalkanes, similar trends with respect to the photolysis mode are displayed: Within the experimental error, the *syn*/*anti*-housane ratios are the same for the elevated-temperature (40 °C) direct (Entry 1) and the *trans*-piperylene-quenched photolysis (Entry 3), while the low-temperature (−75 °C) direct photolysis (Entry 2) gave the same ratios as the benzophenone-sensitized one (Entry 4). For both azoalkanes, the *syn*-housane is slightly preferred (**2a**: 62%; **2b**: 53%; Entry 1) in the direct photolyses as well as in the quenched photolyses at 40 °C (Entry 4). However, a substantial difference is observed between the product ratios for both azoalkanes in the low-temperature direct and sensitized photolysis, for which the *syn*/*anti* ratios are 39:61 for **2a** and 6:94 for **2b** (Entry 4).

The activation parameters for the *syn*-to-*anti* isomerization of the housane **2b** were determined by following the decrease of *syn*-housane at five temperatures in the range from +70 to +110 °C by ^{1}H NMR spectrosopy to be E_a = 26 ± 2 kcal/mol and log A = 12.1 ± 0.9 s^{-1} (see Table 3). The values for the housanes **2a** were previously measured to be E_a = 29 ± 2 kcal/mol and log A = 12.6 ± 0.9 s^{-1}.[7]

Discussion

The azoalkanes **1a** and **1b** are very similar in structure, the only difference lies in the annellated ring, which is cyclopentene in **1a** but cyclopentane in **1b**. Nevertheless, this apparently small structural variation is responsible for a substantial difference in the *syn*/*anti*-housane product ratio of both azoalkanes, provided the photolysis conditions are appropriate. In particular, under singlet conditions (Table 1), i.e., elevated-temperature direct (Entry 1) or quenched (Entry 3) photolysis, both azoalkanes **1a** and **1b** afford in slight preference the thermodynamically less favored (supported by AM1 calculations and complete thermal *syn*-to-*anti* isomerization) inverted *syn* diastereomer (Entries 1 and 3). This is the expected behavior for the photochemical denitrogenation,[1a,1b,5d] which is taken as experimental evidence for the intervention of a singlet diazenyl diradical ^{1}**DZ** in the S_H2 process that leads to the inverted *syn*-**2** housane. As for the effect of the annellated ring, namely cyclopentene

Table 1. Product studies of the photochemical denitrogenation of azoalkanes **1a** and **1b** (the corresponding irradiations of both azoalkanes were run parallel under identical conditions)

Entry	Photolysis conditions[a]	Temperature [°C]	Product ratio[b]	
			syn/*anti* (**2a**)	*syn*/*anti* (**2b**)
1	direct	40	62:38	53:47
2	direct	−75	38:62	6:94
3	quenched	40	65:35	54:46
4	sensitized	40	39:61	6:94

[a] In [D_8]toluene; for the direct and *trans*-piperylene-quenched (1 M) photolyses, the 351-nm (0.8 W) line of the argon-ion laser was used, for the benzophenone-sensitized (1 M) one, the 333-nm (0.6 W) line. [b] Determined by ^{1}H NMR analysis, normalized to 100%, error ±5 of the stated values; hexamethyldisiloxane as internal standard; mass balance ≥ 95%.

in **1a** or cyclopentane in **1b**, backside displacement of N_2 in the respective singlet diazenyl diradicals **^{1}DZ(1a)** and **^{1}DZ(1b)** is essentially insensitive to such structural variation during the inversion process.

In contrast, the photolytic deazetation of the azoalkanes **1** under triplet conditions, i.e., low-temperature direct or benzophenone-sensitized photodenitrogenation, leads to a small preference of the *anti*-**2a** housane from the unsaturated azoalkane **1a** (Entries 2 and 4), while the retention product *anti*-**2b** is formed almost exclusively for the saturated derivative **1b** under the same conditions. The fact that the *anti*-housane (retention) is preferred by far is unusual, since normally the triplet denitrogenation of simple DBH derivatives has furnished about equal amounts of retained (*ret*) and inverted (*inv*) housanes, as shown for a few cases below (Figure 1).[5d] The data show that the *ret*/*inv* ratio of housanes is ca. 50:50, but certainly no preference for retention is expressed. This lack of stereoselectivity of the triplet denitrogenation has been rationalized in terms of a planar nitrogen-free triplet diradical **^{3}DR** (Scheme 1). The low energy barrier (< 3 kcal/mol) for cyclization by intersystem crossing accounts for the small if not negligible substituent effects.[2,10] Thus, the fact that the triplet denitrogenation of the azoalkane **1b** affords almost exclusively (*inv*/*ret* ratio of 6:94) the retained housane *anti*-**2b** is an exception.

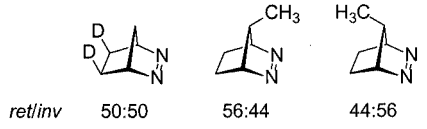
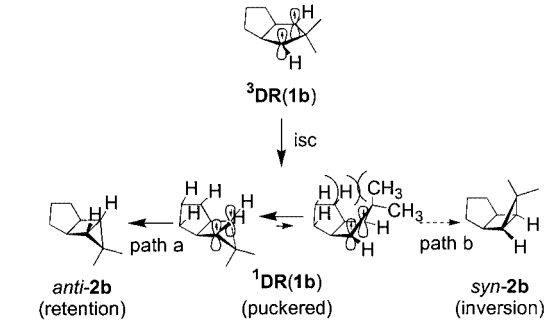


Figure 1. Diastereoselectivity (*ret*/*inv* ratio) for the triplet denitrogenation of simple DBH derivatives

What is the reason for this *anti* stereoselectivity in the triplet pathway? As mentioned before, the significant difference between the azoalkane **1a** and **1b** lies in the annellated ring. This structural variation becomes important during the cyclization of the nitrogen-free planar triplet diradical **^{3}DR** (Scheme 2).[10,11] After intersystem crossing (isc) to the singlet diradical **^{1}DR**, the direction of the ring closure to the diastereomeric housanes **2** is controlled by steric effects between the *gem*-dimethyl-substituted methylene bridge with the annellated ring. This steric interaction is stronger for the bulkier annellated cyclopentane ring during the puckering motion of the ring closure in the resulting **^{1}DR(1b)** diradical such that the *anti*-**2b** (path a) rather than *syn*-**2b** (path b) is generated in high preference (Scheme 2). For the annellated cyclopentene ring in the **^{1}DR(1a)** diradical, the puckering motion is less obstructed during the ring closure to the housane *syn*-**2a** by such steric effects and a relatively large amount of inverted product is obtained (*syn*/*anti* ratio 39:61).

From the *syn*/*anti*-housane ratios of the triplet pathway we may calculate by means of the Arrhenius equation the difference in the energy barriers for the ring closure of the **^{1}DZ** diradical to the two housane diastereomers. The ΔE_a value is 0.24 ± 0.04 kcal/mol for **^{1}DR(1a)** and for **^{1}DR(1b)** it is 1.4 ± 0.3 (Figure 2). The difference in the steric strain



Scheme 2

between the *gem*-dimethyl-substituted methylene bridge and the annellated ring manifests itself not only in the *syn*/*anti* diastereoselectivity of the triplet photolysis, but also in the activation barrier for the thermal *syn*-to-*anti* isomerization of the diastereomeric housanes; it is by ca. 3 kcal/mol smaller for the saturated housane **2b** (Figure 2).

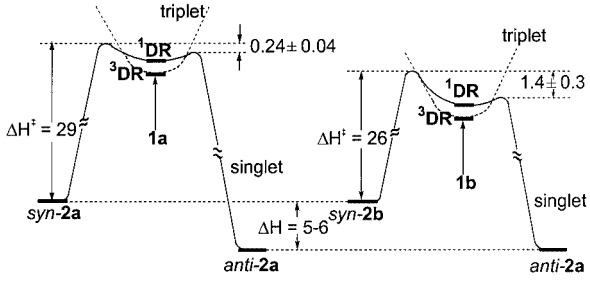


Figure 2. Energy profiles [kcal/mol] for the *syn*/*anti*-housane formation in the thermal *syn*-to-*anti* isomerisation of the housanes **2a**,**b** through the singlet diradical **^{1}DR** (solid curve) and in the triplet-sensitized and direct (−75 °C) photochemical denitrogenation of the azoalkanes **1a**,**b** after isc of the triplet diradical **^{3}DR** (dashed curve)

Conclusion

In summary, in this study we have shown the influence of long-range steric interactions on the *syn*/*anti*-housane distribution in the photolyses of the DBH-type azoalkanes **1a** and **1b**. This steric effect derives from the structural difference between cyclopentene and cyclopentane annellation. While the ring closure of the diazenyl diradical **^{1}DZ** in the S_H2 process (inversion) is relatively insensitive to such remote steric interaction for the direct photolysis (singlet pathway), it promotes cyclization of the planar nitrogen-free **^{3}DR** diradical preferably to the *anti*-housane (retention) in the triplet process. Despite the high degree of retention in this triplet photolysis, this does not constitute a case of "stereochemical memory", as demonstrated for the direct photolysis (singlet) of related bridgehead-substituted cyclopentene-annellated DBH-type azoalkanes,[12] because in the triplet process the planar nitrogen-free triplet diradical **^{3}DR** intervenes, which has lost all of the original stereochemical information. The high *anti* diastereoselectivity of the pre-

sent case is the consequence of remote steric interactions in the transition state for the triplet cyclization ^{3}**DR** → *syn*-**2b**.

Experimental Section

General Aspects: NMR spectra were measured with a Bruker AC200 or AC250 in [D_8]toluene with hexamethyldisiloxane as internal standard. UV absorption spectra were recorded with a Hitachi U 3200 spectrophotometer. Elemental analyses were performed by the Microanalytical Division of the Institute of Inorganic Chemistry (University of Würzburg). Photolyses were carried out at the 333-nm and 351-nm laser lines of a continuous-wave argon-ion laser (INNOVA 100, Coherent Company).

Synthesis of Housane 2b: A sample of (1α,4α,4aα,7aα)-4,4a,5,6,7,7a-hexahydro-8,8-dimethyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazin (**1b**) (50.0 mg, 0.304 mmol) was dissolved in pentane (ca. 0.7 mL), transferred to an NMR tube, deareated by purging with a slow stream of argon for 10 min, and irradiated at the 333-nm, 351-nm and 364-nm lines of the argon-ion laser at 20 °C for ca. 10 min. The pale yellow photolysate was passed through a short column of basic alumina (ca. 2.0 g), the solvent evaporated (20 °C, 20 mbar) and the diastereomeric mixture of housanes **2b** was obtained in quantitative yield as colorless oils, which could not be separated by column chromatography. Thermolysis at elevated temperature (> 90 °C) led to the pure *anti*-**2b** diastereomer. The housane *syn*-**2b** was spectroscopically characterized directly in the mixture of diastereomers.

***endo*-3,3-Dimethyltricyclo[3.3.0.0.^{2,4}]octane (*anti*-2b):** ^{1}H NMR (250 MHz, [D_8]toluene): δ = 0.75 (s, 2 H), 0.87 (s, 3 H, CH_3), 1.19 (s, 3 H, CH_3), 1.30−1.80 (m, 5H), 1.94−2.22 (m, 3 H) ppm. ^{13}C NMR (63 MHz, [D_8]toluene): δ = 14.3 (q), 21.2 (s), 24.6 (q), 25.7 (t), 29.7 (d), 31.7 (t), 38.8 (d) ppm.

Table 2. Product studies of the photochemical denitrogenation of azoalkanes **1a** and **1b** (the corresponding irradiations of both azoalkanes were run in parallel under identical conditions)

Entry	Azoalkane	Photolysis conditions[a]	Temperature [°C]	Time [min]	Conversion (%)[b]	Product ratio[b] *syn*-**2**/*anti*-**2**
1		direct	40	10	> 95	62:38
2		direct	10	10	85	58:42
3		direct	–20	15	82	48:52
4		direct	–50	20	75	41:59
5		direct	–75	30	79	38:62
6		quenched	40	10	94	65:35
7		quenched	–20	15	47	53:47
8	**1a**	quenched	–75	30	11	38:62
9		sensitized	40	20	50	39:61
10		sensitized	–20	30	49	39:61
11		sensitized	–75	60	10	39:61
12		direct	40	10	72	53:47
13		direct	10	10	64	46:54
14		direct	–20	15	72	33:67
15		direct	–50	20	76	15:85
16		direct	–75	30	83	6:94
17		quenched	40	10	59	54:46
18		quenched	–20	15	42	44:56
19	**1b**	quenched	–75	30	12	23:77
20		sensitized	40	20	54	6:94
21		sensitized	–20	30	56	2:98
22		sensitized	–75	60	16	2:98

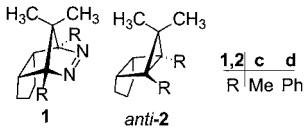
[a] In [D_8]toluene; for the direct and *trans*-piperylene-quenched (1 M) photolyses, the 351-nm (0.8 W) line of the argon-ion laser was used, for the benzophenone-sensitized (1 M), the 333-nm (0.6 W) line. [b] Determined by ^{1}H NMR analysis; normalized to 100%; mass balance ≥ 95%; hexamethyldisiloxane as internal standard; error ±5% of the stated values.

***exo*-3,3-Dimethyltricyclo[3.3.0.0.^{2,4}]octane (*syn*-2b):** ^{1}H NMR (200 MHz, [D_8]toluene): δ = 0.73 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 2.66−2.80 (m, 2 H) ppm; the remaining peaks overlap with signals of the *anti* diastereomer. ^{13}C NMR (50 MHz, [D_8]toluene): δ = 19.3 (q), 24.1 (s), 27.9 (t), 28.6 (d), 32.0 (t), 37.3 (d) ppm; the remaining peaks overlap with signals of the *anti* diastereomer.

Diastereomeric mixture of *syn*/*anti*-2b: IR (neat): $\tilde{\nu}$ = 3012, 2945, 2869, 1454, 1376, 1255, 1117, 1020, 884, 811 cm^{-1}. $C_{10}H_{16}$ (136.2): calcd. C 88.16, H 11.84; found C 87.80, H 12.09.

Product Studies of the Azoalkanes 1: For the direct photolyses, a sample of the azoalkane **1** (**1a**: ca. 0.074 mmol; **1b**: ca. 0.117 mmol; about the same optical density) in [D_8]toluene (0.6 mL) and of hexamethyldisiloxane (2 μL) was transferred to an NMR tube, deareated by purging with a slow stream of argon for 10 min, and irradiated at the 351-nm laser line (0.8 W; widened to ca. 5 cm by a lens) of the argon-ion laser at the temperature specified in Table 2. For the quenching experiments, *trans*-piperylene (1 M) was employed as triplet quencher. In the triplet-sensitized photolyses, benzophenone (1 M) was used as sensitizer and irradiated at the 333-nm laser line (0.6 W). The results are listed in Table 2.

Synthesis and Photolysis of the Azoalkanes 1c and 1d: The saturated azoalkanes **1c** and **1d**, which are Me- and Ph-substituted on the bridgehead positions were prepared as described in the literature.[9,13] Their photolysis afforded under all conditions exclusively the known housanes *anti*-**2c**,**d**.[14]



Determination of Relative Photolysis Quantum Yields of the Azoalkanes 1a,b: The relative quantum yields have been determined by a method which has been used for similar azoalkane derivatives.[15] Aliquots (ca. 2.8 mL) of degassed toluene solutions of azoalkanes **1a** and **1b** (absorbance ca. 0.60 at λ = 351 nm) were placed into UV cuvettes (1 × 1 cm) and irradiated at equal time intervals of ca. 1 s with the 351-nm widened beam of the argon-ion laser. The laser light intensity was adjusted by using the intensity regulation (± 0.05%), supplied by the instrument. The irradiation was conducted up to 7−11 data points per experiment. The decreasing absorbance (A) versus irradiation time was monitored by UV spectrophotometry. The plots of log $[(10^{A}_0 - 1)/(10^{A} - 1)]$ versus irradiation time were linear with correlation coefficients (R^2) greater than 0.98. The relative photoreaction quantum yields (Φ_{rel}) were calculated from the ratio of the slopes S(**1a**)/S(**1b**) = $\varepsilon_{1a}\Phi_{1a}/(\varepsilon_{1b}\Phi_{1b})$, where ε_{1a} and ε_{1b} are the extinction coefficients of the azoalkanes **1a** and **1b** at the irradiation wavelength of 351 nm (ε_{1a} = 174 M^{-1} cm^{-1}; ε_{1b} = 110 M^{-1} cm^{-1}). The relative quantum yields have been determined to be Φ_{rel}(**1a**) = 0.84 ± 0.03·Φ_{rel}(**1b**).

Determination of the Activation Parameters for the Thermal *syn*-to-*anti* Isomerization of the Housane 2b: The activation energies and the log A values for the *syn*-to-*anti* isomerization of the housanes **2** were obtained from the first-order kinetics of the thermolysis of the *syn* diastereomer (a *syn*/*anti* diastereomeric mixture of the housane was used) to the persistent *anti*-housanes (Table 3). The time profile of the amount of *syn*- and *anti*-housanes was determined by ^{1}H NMR spectroscopy as a function of temperature. From this data, the rate constants of isomerzation were evaluated according to first-order kinetics and the activation parameters calculated by means of the Arrhenius equation.

Table 3. Activation parameters for the *syn*-to-*anti* isomerization of the housane **2a** (the amount of *syn*- and *anti*-housanes was determined by ^{1}H NMR spectroscopy with naphthalene as internal standard; error ±5% of the stated values)

Entry	Temperature [°C]	$k \cdot 10^5$ [s^{-1}]	E_a [kcal mol^{-1}]	log A [s^{-1}]
1	70	2.8		
2	80	5.3		
3	90	21.4	26 ± 2	12.1 ± 0.9
4	100	55.3		
5	110	129.4		

Acknowledgments

The generous financial support from the Deutsche Forschungsgemeinschaft, the Volkswagen Stiftung and the Fonds der Chemischen Industrie gratefully appreciated. V. M. is grateful for a Marie-Curie fellowship from the European Commission.

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Received August 29, 2002
[I02484]