(d, 12H; CH$_3$ **3d**), 0.89 (d, 24H; CH$_3$ (**3d**)$_2$); ^{13}C NMR ([D$_8$]toluene): δ = 227.8 (carbene-C **3d**), 119.0 (N$_2$C=CN$_2$ (**3d**)$_2$), 135.8, 121.2, 110.3 (Ar–C **3d**), 142.3, 120.2, 110.1 (Ar–C (**3d**)$_2$), 55.6 (NCH$_2$ **3d**), 55.8 (NCH$_2$ (**3d**)$_2$), 29.4 (*C*HMe$_2$ **3d**), 26.1 (*C*HMe$_2$ **3d** = **3d**), 20.5 (CH$_3$ **3d**), 20.9 (CH$_3$ (**3d**)$_2$).

3c: Yellow crystals (m.p. 37 °C); ^{1}H NMR (C$_6$D$_6$): δ = 7.18 (m, 4H; Ar–H), 6.08 (m, 4H; Ar–H), 4.52 (s, br, 4H; NCH$_2$), 4.11 (s, 4H; NCH$_2$), 0.97 (s, 18H; C(C*H*$_3$)$_3$), 0.81 (s, 6H; C(C*H*$_3$)$_2$); ^{13}C NMR (C$_6$D$_6$): δ = 119.5 (N$_2$C=CN$_2$), 141.9, 141.8, 120.1, 119.4, 108.8, 105.8 (Ar–C), 58.6 (NCH$_2$), 22.4 (NCH$_2$), 36.7 (*C*Me$_3$), 33.6 (*C*Me$_2$), 29.4 (C(*C*H$_3$)$_3$), 25.0 (C(*C*H$_3$)$_2$).

5: A solution of [Mo(nor)(CO)$_4$] (300 mg, 1.0 mmol) was added dropwise to a solution of **3c** (336 mg, 0.80 mmol) in THF (30 mL) under argon. The yellow reaction solution was stirred for 12 h at ambient temperature. The solvent was removed in vacuo and the residue was dissolved in ethyl acetate (3 mL). This solution was purified by chromatography (SiO$_2$, hexane/ethyl acetate 5/1) and the product solution was reduced in volume, yielding yellow crystals of **5**. Yield 402 mg (80 %). ^{1}H NMR (CDCl$_3$): δ = 7.53–7.22 (m, 8H; Ar–H), 5.55, 4.93, 4.32, 3.91 (d, 2H; NC*H*$_2$), 1.10 (s, 18H; C(C*H*$_3$)$_3$), 0.88 (s, 6; C(C*H*$_3$)$_2$); ^{13}C NMR (CDCl$_3$): δ = 219.9 (*trans*-CO), 210.0 (*cis*-CO), 208.2 (carbene-C), 136.4, 135.9, 122.6, 122.2, 113.2, 110.8 (Ar–C), 59.1, 52.4 (NCH$_2$), 41.0 (*C*Me$_2$), 35.0 (*C*Me$_3$), 29.6 (C(*C*H$_3$)$_3$), 24.8 (C(*C*H$_3$)$_2$).

Received: June 7, 1999
Revised: August 18, 1999 [Z13519]

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[19] X-ray structure analysis: All data sets were collected on a Enraf-Nonius CAD4 or a Nonius Kappa-CCD diffractometer with a rotating anode FR591 (Nonius) used as a radiation source. The following programs were used: EXPRESS and COLLECT for data collection; MolEN and Denzo-SMN for data reduction; SORTAV for absorption correction of CCD-Data; SHELXS-97 for structure solution; SHELXL-97 for structure refinement; and SCHAKAL-92 for molecular graphics. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-124994 (**3c**), -124995 (**3d**)$_2$ and -124996 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033, e-mail: deposit@ccdc.cam.ac.uk). a) **3c** (C$_{29}$H$_{40}$N$_4$): $M_r = 444.65$, colorless crystals 0.30 × 0.30 × 0.15 mm, $a = 19.155(1)$, $b = 0.534(1)$, $c = 15.439(1)$ Å, $\beta = 123.92(1)°$, $V = 1585.1(3)$ Å^3, $\rho_{calcd} = 1.142$ g cm^{-3}, $\mu = 0.68$ cm^{-1}, empirical absorption correction ($0.980 \leq T \leq 0.990$), $Z = 4$ (C16 and midpoint of the C2–C2* bond on a twofold axis), monoclinic, space group $C2/c$ (No. 15), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 9982 measured reflections ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.71$ Å^{-1}, 3884 unique and 3070 observed reflections $[I \geq 2\sigma(I)]$, 184 refined parameters, $R = 0.047$, $wR^2 = 0.117$, max. (min.) residual electron density 0.28 (−0.17) e Å^{-3}, positional disorder of the bridging atoms C15, C16 and C17, hydrogen atoms calculated and refined as riding atoms. b) **3d** (C$_{30}$H$_{44}$N$_4$): $M_r = 460.69$, yellow crystals, 0.30 × 0.20 × 0.10 mm, $a = 10.558(3)$, $c = 24.577(7)$ Å, $V = 2739.6(13)$ Å^3, $\rho_{calcd} = 1.117$ g cm^{-3}, $\mu = 4.99$ cm^{-1}, no absorption correction ($0.865 \leq T \leq 0.952$), $Z = 4$ (C2–C12 bond on twofold axis), tetragonal, space group $P4_32_12$ (No. 96), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 3162 measured reflections ($+h$, $-k$, $-l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 2802 unique and 1953 observed reflections $[I \geq 2\sigma(I)]$, 160 refined parameters, $R = 0.060$, $wR^2 = 0.160$, max. (min.) residual electron density 0.32 (−0.27) e Å^{-3}, Flack parameter 0.0(11), hydrogen atoms calculated and refined as riding atoms. c) **5** (C$_{33}$H$_{40}$N$_4$O$_4$Mo): $M_r = 652.63$, yellow crystals, 0.35 × 0.30 × 0.25 mm, $a = 17.637(1)$, $c = 20.517(1)$ Å, $V = 6382.1(6)$ Å^3, $\rho_{calcd} = 1.358$ g cm^{-3}, $\mu = 4.53$ cm^{-1}, empirical absorption correction ($0.858 \leq T \leq 0.895$), $Z = 8$ (C16 and Mo on a twofold axis), tetragonal, space group $P4_2/nbc$ (No. 133), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ-scans, 17302 measured reflections ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.71$ Å^{-1}, 4888 unique and 3515 observed reflexions $[I \geq 2\sigma(I)]$, 195 refined parameters, $R = 0.055$, $wR^2 = 0.126$, max. (min.) residual electron density 0.50 (−0.76) e Å^{-3}, hydrogen atom positions calculated and refined as riding atoms.

[20] Note added in proof (December 21, 1999): The thermal dissociation of sterically less-demanding dibenzotetraazafulvalenes was recently demonstrated by Lemal et al. on the basis of NMR data. See Y. Liu, P. E. Linder, D. M. Lemal, *J. Am. Chem. Soc.* **1999**, *121*, 10626.

Chromophore Alignment in a Chiral Host Provides a Sensitive Test for the Orientation–Intensity Rule of Induced Circular Dichroism**

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Circular dichroism is an essential spectral property for probing chirality.[1, 2] An interesting effect arises when an achiral guest chromophore is complexed in a chiral host. The guest becomes optically active, a phenomenon referred to as "induced" circular dichroism (ICD).[3–5] The spectroscopic information resulting from this interaction is unique, since sign and magnitude of the ICD signal depend on the relative orientation of the chromophore in the host. Harata et al. have

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[**] This work was supported by the Swiss National Science Foundation and the Fonds der Chemischen Industrie. We thank Dr. G. Scherer, Institute of Organic Chemistry, as well as A. Merz and T. Schultheiss, Institute of Biophysical Chemistry, for assistance with the NMR-ROESY and ICD measurements.

developed a rule for the inclusion complexes of cone-shaped chiral hosts like cyclodextrins (CDs).[6] According to this rule, a positive ICD signal arises when the electric transition dipole moment is aligned parallel to the axis of the host, but the signal is negative and half as strong when it is oriented in a perpendicular manner (Figure 1).[2, 5] More recently, a similar rule has also been developed for ICD effects outside the host cavity,[7] where the sign of the ICD signal is opposite to that arising inside the host cavity, and a refined computational treatment for ICD effects has been introduced.[8, 9]

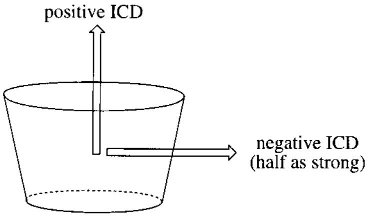
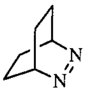


Figure 1. Dependence of the sign and intensity of the induced circular dichroism (ICD) effect on the direction of the electric transition dipole moment of the guest in CD inclusion complexes.

Knowledge of the relative orientation of the guest in host–guest complexes, in particular when weak van der Waals interactions operate,[4] is important for the development of functional supramolecular materials, such as those for catalytic or analytical purposes. Crystal structure determination may provide accurate data for CD complexes in the solid state.[10, 11] Structural information for host–guest complexes in solution, however, is accessible only in limiting cases. Although recent advances in the interpretation of NMR data open new opportunities along this line,[12] relative orientations of host–guest complexes have often been assigned by ICD effects.[5] Harata's rule, which provides a qualitative basis for structural interpretations of ICD effects, has been examined by shifting the electronic transitions in benzene and naphthalene through substituents[6, 13–16] while maintaining the (axial) orientation of the guest. These sophisticated "photophysical tests" have provided strong support for the rule.

The simplest and perhaps most intuitive test of Harata's rule would involve a flip of a chromophore within the chiral CD cavity. Such a change of the alignment of the same chromophore within the same host from parallel to perpendicular should not only invert the sign of the ICD signal, but also provide a promising test for the predicted strength of the ICD effect (see Figure 1). This "structural test" has not been performed to our knowledge. Hence, our present finding of a weaker and inverted ICD effect upon going from the β-CD complex of azoalkane **1** to that of the sterically modified derivative **2** should be of interest. Variations in the sign of the ICD effect have been previously observed by using different hosts, for example, β-CD and γ-CD.[17, 18] However, the required deep inclusion, shown by Figure 1,[6, 7] has not been experimentally established in these studies. For azoalkanes **1** and **2**, complete immersion in the CD cavity can be proven by NMR measurements.



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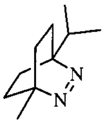

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Initial evidence for 1:1 complexation of azoalkane **1** by β-CD was obtained in the course of a recent fluorescence study.[19] Azoalkane **1** and the derivative **2** exhibit high binding constants with β-CD in water (both ca. $1000\,\text{M}^{-1}$).[20] The mode of association has now been established by means of NMR 2D-ROESY spectra. These revealed selective NOE enhancements between both the inner CD protons (H-3 and H-5) and all the protons of azoalkanes **1** and **2**. This provides evidence for the formation of a deep inclusion complex. The protons which displayed intermolecular cross peaks in the ROESY spectra were also the ones which exhibited chemically induced NMR shifts (CIS). Interestingly, the CIS values of the guest molecules provided a first indication for different modes of inclusion of azoalkanes **1** and **2**. Namely, the CIS values for the comparable *syn* and *anti* protons of azoalkane **2** were significantly smaller than those for **1** and, strikingly, those for the *syn* protons had opposite signs (Figure 2).

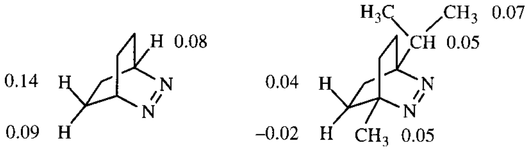

Figure 2. CIS values for inclusion of azoalkanes **1** and **2** into β-CD.

Further insight into the specific modes of inclusion in β-CD was obtained by force-field calculations.[21] Azoalkane **1** has a nearly spherical shape of about 5 Å diameter, which renders several modes of inclusion in the β-CD cavity (diameter range 6–6.5 Å) feasible. AMBER calculations produced four principal conformations for azoalkane **1** in β-CD, which can be referred to as lateral, frontal, apical, and basal inclusions (Figure 3a). The apical inclusion had the lowest potential energy, but the energetic difference to the lateral and basal conformation was small (within $1.5\,\text{kcal}\,\text{mol}^{-1}$). Only the frontal inclusion appeared to be significantly disfavored by $3.1\,\text{kcal}\,\text{mol}^{-1}$. Simulations using molecular dynamics[21] retained the four principal conformations. In contrast, the selection of MM+ as an alternative force field caused the energy minima of the basal and frontal inclusions to disappear, leaving only the apical and lateral conformations as viable geometries, with the latter only $1.0\,\text{kcal}\,\text{mol}^{-1}$ higher in energy.

The dimension of azoalkane **2** along its long axis (about 8 Å) exceeds the cavity diameter of β-CD significantly. This renders only the frontal mode of inclusion feasible for **2**, and accordingly a strong preference for this conformation ($> 10\,\text{kcal}\,\text{mol}^{-1}$) was obtained by the AMBER calculations. A marginal preference ($0.6\,\text{kcal}\,\text{mol}^{-1}$) for the conformation with the larger isopropyl group penetrating into the cavity was found (Figure 3b).

More definitive evidence for the inclusion geometries was obtained from the ICD signals of the characteristic azo n → π* absorption in the near UV. Although azoalkanes **1** and **2** showed very similar absorption maxima (ca. 375 nm) and extinction coefficients (ca. $55\,\text{M}^{-1}\,\text{cm}^{-1}$) in their β-CD complexes, they gave rise to opposite ICD effects, namely positive

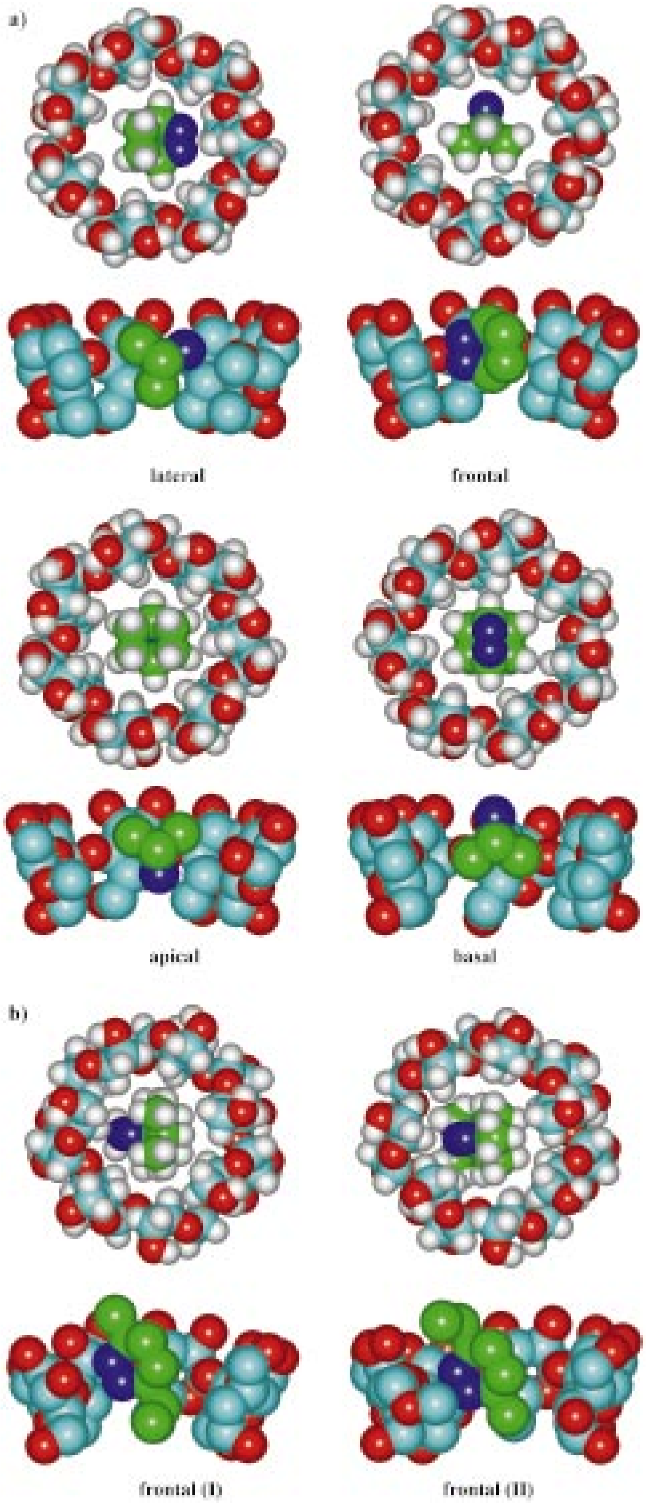

Figure 3. AMBER-optimized β-CD inclusion complexes. a) Azoalkane **1**: Upper views are from the wider rim, and the lower views are intersections from the side (hydrogen atoms removed for clarity); b) azoalkane **2**: Upper views are from the narrower rim, and the lower views are intersections from the side (hydrogen atoms removed for clarity). Shown for (b) are the two frontal modes of inclusion with the isopropyl (I) and the methyl group (II) entering the cavity.

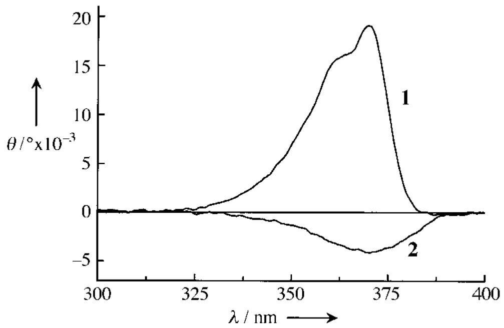

Figure 4. ICD spectra for azoalkanes **1** and **2** (4.0 mM) in the presence of β-CD (12.0 mM) in D_2O.

for **1** and negative as well as significantly weaker for **2** (Figure 4). Since both azoalkanes display similar binding constants and form deep inclusion complexes, as corroborated by the ROESY spectra, this marked variation can only be interpreted in terms of different modes of inclusion. This interpretation is supported by the results from molecular modeling (Figure 3) and the observed CIS values (Figure 2).

According to Harata's rule, a positive ICD effect is expected for a parallel alignment of the electric transition dipole moment relative to the CD axis, while a negative effect should result from a perpendicular alignment (Figure 1). The $n \rightarrow \pi^*$ transition moment of *cis*-azoalkanes points along the p orbitals of the azo π-system. This direction can be readily determined by simple multiplication of the relevant signs of the lobes of the pertinent n_- and π^* orbitals as illustrated in Figure 5. Consequently, one expects a negative ICD effect for the apical, basal, as well as the frontal inclusion modes (Figure 1) due to the perpendicular alignment of the transition moment. The negative ICD signal for azoalkane **2** is, thus, in agreement with the frontal inclusion, which is the only sterically feasible one. The positive ICD signal for azoalkane **1** must arise from the lateral conformation, which is the only one to ensure a nearly parallel orientation of the transition moment. Also noteworthy is that the intensity of the ICD signal for azoalkane **1** is significantly stronger than that for **2**, as expected from Harata's rule. However, although the chromophore characteristics remain the same, the experimental effect is more pronounced than that predicted by theory (a factor of four to five versus two).

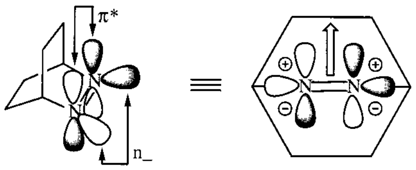

Figure 5. Determination of the electric transition dipole moment for the lowest $n \rightarrow \pi^*$ electronic transition of azoalkanes **1** and **2** by formal multiplication of the orbital lobes of the involved n_- and π^* orbitals. The vector pointing from the resulting region of electron deficiency ⊖ to that of electron excess ⊕ provides the direction of the electric transition dipole moment.

In summary, this work provides an example for a conformational assignment of host–guest complexes in solution. The ICD effects predicted by Harata's rule are actually observed for azoalkanes **1** and **2**, for which two different modes of inclusion in a CD apply. We consider these results as a sensitive test case of Harata's rule, since the transition moment of the localized azo chromophore is insensitive to the alkyl substitution pattern. The present "structural test" is distinct, compared to earlier studies,[6, 13–16] since a whole chromophore is actually flipped around in the chiral cavity. Most importantly and in contrast to related studies,[17, 18] different orientations of the same chromophore (−N=N−) could be explored within the same host (β-CD).

Experimental Section

β-CD (Fluka) and >99.8% D_2O (Glaser AG, Basel, Switzerland) were used as received. All experiments were performed at ambient temperature in D_2O for consistency with the NMR measurements. The azoalkane **2** was synthesized by cycloaddition of α-terpinene with *N*-methyltriazolinedione (both from Aldrich), subsequent hydrogenation, hydrolysis, and oxidation, in analogy to literature methods for the known azoalkane **1**.[22]

2: M.p. 34–35 °C; UV (D_2O): $\lambda_{max} = 373$ nm ($\varepsilon = 54\,cm^{-1}M^{-1}$); ^1H NMR (300 MHz, D_2O): $\delta = 2.43$ (sept, 1H, $J = 6.9$ Hz), 1.74 (s, 3H), 1.54–1.51 (m, 4H, *anti*), 1.24 (d, 6H, 6.9 Hz), 1.11–1.08 (m, 4H, *syn*); ^{13}C NMR (75 MHz, D_2O): $\delta = 69.03$, 63.75, 34.50, 28.74, 25.33, 23.70, 17.81; GC–MS [column SE-30, 70 °C (for 10 min)–10 K min^{-1}–270 °C (for 10 min)]: 13.82 min; MS: 166.16 (M^+), 138 ($M^+ - N_2$), 123 (138 − CH_3), 109, 95 (138 − iC_3H_7), 81, 67, 55, 41; elemental analysis calcd for $C_{10}H_{18}N_2$ (%): C 72.24, H 10.91, N 16.85; found: C 72.13, H 10.68, N 17.08.

ICD spectra were recorded with a Jasco J-720 circular dichrograph (0.2 nm resolution, 25 accumulations, 1 cm cell). Blank measurements of D_2O and solutions of β-CD, **1**, and **2** provided no ICD effects in the region examined. The ^1H NMR (300 MHz) CIS values were determined under conditions of nearly quantitative (>90%) complexation (2.5 mM azoalkane, 8.8 mM β-CD). 2D-ROESY spectra (600 MHz) were obtained for solutions of 9.6 mM azoalkane and 4.6 mM β-CD in D_2O.

Received: July 30, 1999 [Z13807]

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[20] The presence of a fluorescent chromophore in azoalkanes **1** and **2** and their water solubility allow the determination of binding constants (unit M^{-1}) with β-CD by several independent techniques. Values of 1100 ± 300, 900 ± 100, 700 ± 300 (ref. [19]), and 920 ± 100 (this work) for azoalkane **1**, and 900 ± 150, 1070 ± 60, 750 ± 200, and 830 ± 150 (all this work) for azoalkane **2** were determined from NMR, UV, fluorescence, and ICD spectroscopy, respectively. The quantitative analysis of these data corroborates the formation of 1:1 complexes.

[21] Calculations were carried out with HyperChem 5.0 (Hypercube Inc). The AMBER-S parameterization for saccharides was employed, see: S. W. Homans, *Biochemistry* **1990**, *29*, 9110–9118. The rigid azoalkanes **1** and **2** were kept frozen in the AM1-optimized geometries. Molecular dynamics calculations were performed according to an established protocol for simulated annealing, see: G. Fronza, A. Mele, E. Redenti, P. Ventura, *J. Org. Chem.* **1996**, *61*, 909–914.

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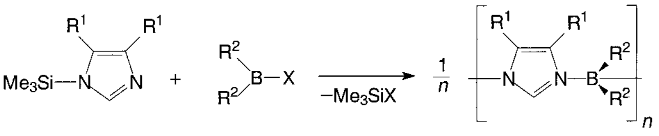
Macrocyclic Imidazolylboranes**

Andre Weiss, Hans Pritzkow, and Walter Siebert*

Dedicated to Professor Gerhard Fritz
on the occasion of his 80th birthday

Polymeric structures have been described for 1-imidazolyldiethylborane[1a] and 1-imidazolyldiphenylborane,[1b] in which a chainlike arrangement results from intermolecular N→B donor/acceptor interactions. An analogous behavior is observed in the cyanoborane $(NC{-}BH_2)_n$ synthesized from $NaBH_3CN$ and HCl.[2] Besides polymeric compounds cyclic cyanoboranes were found consisting of four to ten monomers and showing a maximum of product distribution at $n = 5$. In the following we report on macrocyclic imidazolylboranes.

Initial evidence for the formation of macrocyclic imidazolylboranes occurred in an attempt to prepare bis(3-borane-imidazolyl)boranes from 1-trimethylsilyl-3-borane-imidazole and $RBCl_2$ ($R = NiPr_2$, C_6H_5). Astonishingly, the mass spectra of the products contained a signal group around *m*/*z* 319 and indicated tetrameric imidazolylborane **3a**. Therefore we allowed 1-trimethylsilylimidazole (**1a**) to react with the chloroborane **2a** under high dilution and obtained a mixture of oligomeric imidazolylboranes.



1	**a**	**b**
R1	H	Me

2	**a**	**b**
R2	H	Me
X	Cl	Br

	3a	**b**	**4a**	**b**	**5a**	**6**
R1	H	H	H	H	Me	Me
R2	H	H	Me	Me	H	Me
n	4	5	4	5	4	>5

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[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB 247).