

Figure 3. MALDI-TOF mass spectrum for **9** with a 5'-O-DMT protecting group. Spectral parameters: negative-ion spectrometry, reflector mode, accelerating voltage 20 kV, delay 100 ns, 60 scans averaged.

Experimental Section

The detailed reaction conditions for synthesis of unlabeled compounds **1**, **3**, **5**, **6**, **7** and **8**, their full characteristics and chromatographic conditions for separation of **1a–d** into pure diastereomers were published elsewhere.^[9, 18] The ¹⁸O-labeled water (95 atom % ¹⁸O) was supplied by ICON Services, Inc. (Summit, NJ). The FAB mass spectra were recorded on a Finnigan MAT 95 spectrometer (Bremen, Germany) in negative-ion mode. High-resolution MALDI-TOF mass spectrometry (negative ion spectrometry) was performed with a Voyager-Elite mass spectrometer (PerSeptive Biosystems Inc., Framingham, MA) operating in the reflector mode.

Received: September 26, 2000 [Z15859]

- [1] F. Eckstein, *Antisense Nucleic Acid Drug Dev.* **2000**, *10*, 117–121, and references therein.
- [2] W. J. Stec, A. Wilk, *Angew. Chem.* **1994**, *106*, 747–761; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 709–722.
- [3] P. Guga, M. Koziolkiewicz, A. Okruszek, W. J. Stec in *Applied Antisense Oligonucleotide Technology* (Eds.: C. Stein, A. Krieg), Wiley, New York, **1998**, pp. 23–50.
- [4] R. P. Iyer, D. Yu, N.-H. Ho, W. Tan, S. Agrawal, *Tetrahedron: Asymmetry* **1995**, *6*, 1051–1054; R. P. Iyer, D. Yu, T. Devlin, N.-H. Ho, W. Tan, S. Agrawal, *J. Org. Chem.* **1995**, *60*, 5388–5389; R. P. Iyer, M.-J. Guo, D. Yu, S. Agrawal, *Tetrahedron Lett.* **1998**, *39*, 2491–2494.
- [5] A. Wilk, A. Grajkowski, L. R. Phillips, S. L. Beaucage, *J. Am. Chem. Soc.* **2000**, *122*, 2149–2156.
- [6] C. A. Brautigam, T. A. Steitz, *J. Mol. Biol.* **1998**, *277*, 363–377.
- [7] M. Koziolkiewicz, A. Krakowiak, M. Kwinkowski, M. Boczkowska, W. J. Stec, *Nucleic Acids Res.* **1995**, *23*, 5000–5005.
- [8] M. Koziolkiewicz, A. Krakowiak, A. Owczarek, M. Boczkowska in *RNA Biochemistry and Biotechnology* (Eds.: J. Barciszewski, B. Clark), Kluwer, Dordrecht, **1999**, pp. 315–324.
- [9] W. J. Stec, B. Karwowski, M. Boczkowska, P. Guga, M. Koziolkiewicz, M. Sochacki, M. Wiczorek, J. Błaszczyk, *J. Am. Chem. Soc.* **1998**, *120*, 7156–7167.
- [10] P. A. Frey, R. D. Sammons, *Science* **1985**, *228*, 541–545.
- [11] T. James, UCSF, CA, personal communication.

- [12] S. L. Buchwald, D. E. Hansen, A. Hassett, J. R. Knowles in *Methods in Enzymology* (Ed.: D. L. Purich), Academic Press, New York, **1982**, pp. 279–301.
- [13] B. A. Connolly, F. Eckstein, A. Pingoud, *J. Biol. Chem.* **1984**, *259*, 10760–10763.
- [14] V. Cepus, A. J. Scheidig, R. S. Goody, K. Gerwert, *Biochemistry* **1998**, *37*, 10263–10271.
- [15] K. Hayashi, *Macromolecules* **1970**, *3*, 5–9.
- [16] J. Baraniak, K. Lesiak, M. Sochacki, W. J. Stec, *J. Am. Chem. Soc.* **1980**, *102*, 4533.
- [17] M. Cohn, A. Hu, *J. Am. Chem. Soc.* **1980**, *102*, 913.
- [18] B. Karwowski, P. Guga, A. Kobylańska, W. J. Stec, *Nucleosides Nucleotides* **1998**, *17*, 1747–1759.
- [19] A. Okruszek, P. Guga, W. J. Stec, *Nucleic Acids Symp. Ser.* **1984**, *14*, 267.
- [20] R. L. Jarvest, G. Lowe, B. V. L. Potter, *J. Chem. Soc. Perkin Trans. 1* **1981**, 3186–3195.

Chiral Recognition in Bis-Urea-Based Aggregates and Organogels through Cooperative Interactions**

Maaïke de Loos, Jan van Esch,* Richard M. Kellogg, and Ben L. Feringa*

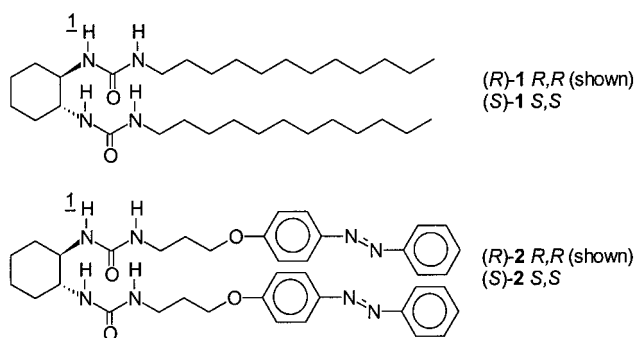
Chiral recognition is indisputably one of the most intriguing phenomena in nature. In chemistry, it is a key feature in applications such as enantioselective catalysis,^[1] separation techniques,^[2] and in the formation of supramolecular systems, both in solid assemblies^[2, 3] and in solution.^[2, 4–6]

Intermediate to solid- and solution-phase systems one might place organogels.^[7, 8] These consist of molecules, self-assembled into large fiberlike aggregates which intertwine to form a reversible gel in organic solvents. Especially the rationally designed 1,2-bis(ureido)cyclohexane derivatives were found to be highly effective gelators for organic solvents.^[9, 10] Furthermore, these compounds contain two stereogenic centers, which for **1** are expressed in the formation of twisted fibers in ethanol with a helicity that depends on the handedness of **1**.^[10b] Related chiral phenomena are found for other gel systems.^[3, 7, 8a,d]

Here we report on chiral recognition through cooperative interactions between aggregates and gels of **1** and a co-aggregating guest **2**.^[11] Guest **2** exhibits the same bis(ureido)-cyclohexane skeleton as **1**, but azobenzene chromophores have been attached to the side chains to differentiate **2** from host **1** and to probe the microenvironment by spectroscopic methods.

[*] Dr. J. van Esch, Prof. Dr. B. L. Feringa, M. de Loos, Prof. Dr. R. M. Kellogg
Department of Organic and Molecular Inorganic Chemistry
Stratingh Institute, University of Groningen
Nijenborgh 4, 9747 AG Groningen (The Netherlands)
Fax: (+31) 50-3634296
E-mail: J.v.Esch@chem.rug.nl, Feringa@chem.rug.nl

[**] This work was supported by the Dutch Foundation for Scientific Research (NWO). The Royal Netherlands Academy of Sciences is gratefully acknowledged for a fellowship to J.v.E.



^1H NMR measurements on solutions of **1** in CDCl_3 showed a strong downfield shift of the NH1 proton upon increasing the concentration, which is indicative of self-association through intermolecular hydrogen bonding (Figure 1).^[12]

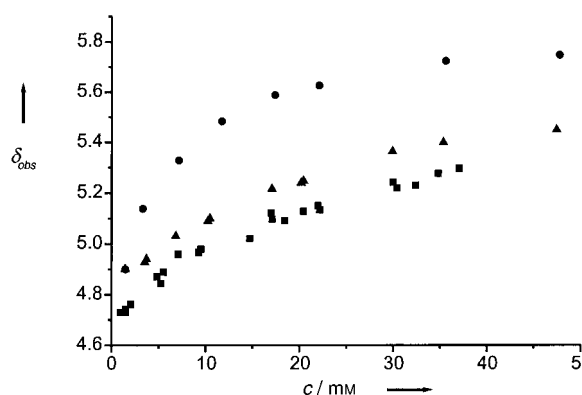
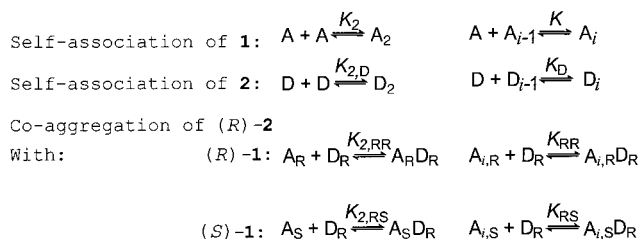


Figure 1. Chemical shifts plotted against the total urea concentration for: NH1 of pure **1** (■), NH1 of (*R*)-**2** in (*S*)-**1** (●), and NH1 of (*R*)-**2** in (*R*)-**1** (▲; CDCl_3 , $T = 50^\circ\text{C}$). (*R*)-**2** was kept at a fixed concentration of 2 mM and the concentration of either (*S*)-**1** or (*R*)-**1** was increased.

The concentration dependency of the chemical shifts could not be described by a dimerization model,^[13] and indicates that higher aggregates were formed. Thus, in accordance with an earlier study on the self-association of mono-urea compounds^[14] the association equilibria of **1** were treated with a cooperative association model in which all but the first association constant K_2 are assumed to be the same (Scheme 1).^[15, 16] The concentration dependency of the chem-



with $K_2 \neq K_3 = K_4 = \dots = K_i = K$

Scheme 1. Cooperative model for a chiral self-associating system (A) and the co-aggregation of a second chiral molecule (D) with both enantiomers of this system.^[16]

ical shifts can now be described with Equation (1),^[15, 16] and gives the association constants shown in Table 1.

$$\frac{(1 - P_f)^{1/2}}{(2P_f - 1)c^{1/2}} = K_2^{1/2} + K \frac{P_f[(1 - P_f)c]^{1/2}}{2P_f - 1} \quad (1)^{[16]}$$

with

$$P_f = \frac{\delta_a - \delta_{\text{obs}}}{\delta_a - \delta_m}$$

Table 1. Calculated association constants and downfield shifts from the ^1H NMR measurements (CDCl_3 , $T = 50^\circ\text{C}$).

Sample	Calculated for	K_2 [M^{-1}]	K [M^{-1}]	$\Delta\delta_{\text{obs}}^{[a]}$
1	1	25 ± 10	179 ± 18	0.55
(<i>R</i>)- 2 in (<i>R</i>)- 1	(<i>R</i>)- 1	4 ± 1	176 ± 13	0.48
	(<i>R</i>)- 2	5 ± 1	175 ± 17	0.51
(<i>R</i>)- 2 in (<i>S</i>)- 1	(<i>S</i>)- 1	4 ± 1	167 ± 10	0.47
	(<i>R</i>)- 2	6 ± 1	321 ± 21	0.82

[a] $\Delta\delta_{\text{obs}} = \delta_{\text{obs}}(2 \text{ mM}) - \delta_{\text{obs}}(35 \text{ mM})$.

It is clear that the association constant K for the higher aggregates is considerably larger than the dimerization constant K_2 , which indicates that self-association of **1** is indeed a highly cooperative process. This proposal is also supported by variable temperature ^1H NMR measurements: it was found that gelation occurred within 1°C upon cooling a solution at $c > 8 \text{ mM}$.

Co-aggregation of **2** with solution-phase aggregates of (*R*)-**1** or (*S*)-**1** was studied by ^1H NMR titration experiments in which the concentration of **2** was kept constant. Both the NH protons of **1** and **2** could be distinguished. Increasing the concentration of either (*R*)-**1** or (*S*)-**1** caused a downfield shift of the NH1 proton of (*R*)-**2** (Figure 1). Separate FT-IR and ^1H NMR measurements^[17] showed that self-association of **2** is negligible at low concentrations; thus it can be concluded that the downfield shift is the result of co-aggregation of **2** with **1**. CD spectroscopic studies (see below) support this conclusion.

Calculation of the association constants of **1** in the presence of small amounts of (*R*)-**2** revealed that for (*R*)-**1** and (*S*)-**1** the dimerization constants K_2 decreased, but the higher association constants K did not significantly change (Table 1). In contrast, a large difference is observed in the curve shape (Figure 1) and magnitude of the downfield shifts ($\Delta\delta_{\text{obs}}$) when the co-assembly of (*R*)-**2** with (*R*)-**1** and with (*S*)-**1** is compared (Table 1). This observation indicates that both the association constants and the hydrogen-bonded structure in the co-aggregates are dissimilar.

The association constants for the co-assembly of (*R*)-**2** with (*R*)-**1** ($K_{2,RR}$, K_{RR}) and (*R*)-**2** with (*S*)-**1** ($K_{2,RS}$, K_{RS} ; Scheme 1) are also given in Table 1.^[18] For both co-assemblies it can be seen that, as for pure **1**, K_2 is considerably smaller than K , which is indicative of a highly cooperative association process. Furthermore, the dimerization constants $K_{2,RR}$ and $K_{2,RS}$ are of the same magnitude. However, the association constant K_{RS} is almost twice as large as K_{RR} , which indicates that the incorporation of (*R*)-**2** in higher aggregates of (*S*)-**1** is preferred to incorporation in higher aggregates of (*R*)-**1**. Dimerization is apparently not affected by the chirality of the compounds, whereas formation of larger aggregates results in

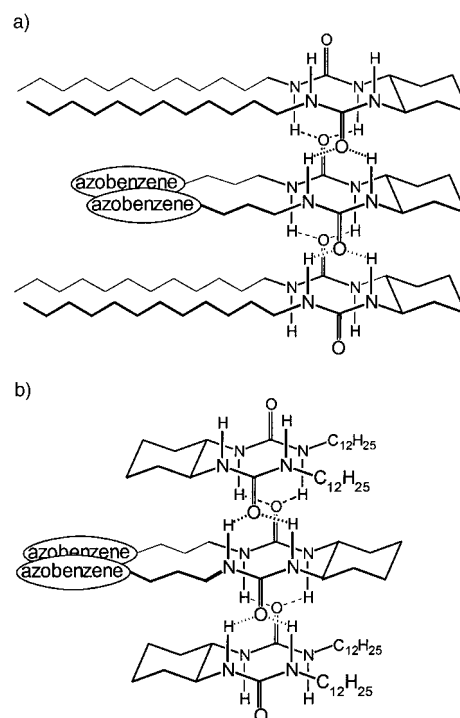
discrimination between the enantiomers. Thus, cooperativity is important for the chiral recognition in these systems. Furthermore, the K_{RR} and $\Delta\delta_{\text{obs}}$ values for the co-assembly of (*R*)-**2** with (*R*)-**1** are similar to those for pure (*R*)-**1**, which indicates they have a comparable hydrogen-bonded structure and strength. However, both the K_{RS} and $\Delta\delta_{\text{obs}}$ values are different for the co-assembly of (*R*)-**2** with (*S*)-**1**, which leads to the conclusion that an aggregate is formed with a different hydrogen-bonded structure and strength.

Chiral recognition in larger aggregates, namely, the gel, was studied by spectroscopic methods and *cis-trans* isomerizations. UV/Vis spectra of solutions of **2** in 1-butanol (0.3 mM) showed strong absorption bands at 238 and 344 nm and a weak band at 440 nm. Incorporation of (*R*)-**2** in 1-butanol gels of (*R*)-**1** or (*S*)-**1** resulted in symmetric absorption bands at 239, 345, and 443 nm, thus indicating the presence of molecularly dispersed azobenzenes.^[19]

CD measurements on pure **2** showed a split CD Cotton effect associated with the UV band at 344 nm for the solvents tested, with the intensity increasing upon decreasing solvent polarity (Figure 2a). The observed exciton coupling exhibits no concentration dependency and thus has to be the result of an intramolecular stacking of the chromophores. The sign of the Cotton effects for (*R*)-**2** and (*S*)-**2** is in agreement with the absolute configuration at the cyclohexane ring.^[20]

The CD spectra of (*R*)-**2** (0.3 mM) in a 1-butanol gel of (*S*)-**1** (18.6 mM) showed a slightly more intense CD effect at room temperature than that of a solution of (*R*)-**2** in 1-butanol (Figure 2). At 45 °C, above the melting point of the gel, the CD effect decreases to a value comparable to that of the solution of (*R*)-**2** in 1-butanol. The change in the CD spectra indicates that (*R*)-**2** becomes incorporated in (*S*)-**1** upon

gelation of (*S*)-**1**. Moreover, the solvent dependency suggests that the slight increase in intensity arises from the environment of (*R*)-**2** being less polar when it is incorporated in the gel of (*S*)-**1** than in 1-butanol itself (Scheme 2b).



Scheme 2. Model for the incorporation of **2** in a) an aggregate of **1** with the same configuration (shown: (*R*)-**2** in (*R*)-**1**) or b) an aggregate of **1** with opposite configuration (shown: (*R*)-**2** in (*S*)-**1**, showing the distinct environments for the azobenzene groups.

In contrast, incorporation of (*R*)-**2** in a gel of (*R*)-**1** results in a strong positive CD effect, from which the exciton coupling has disappeared (Figure 2b). Apparently, (*R*)-**2** has adopted a different conformation upon co-aggregation with (*R*)-**1**; the azobenzene groups are no longer stacked but incorporated between the close-packed alkyl chains of (*R*)-**1** (Scheme 2a). As for (*S*)-**1**, the solution-phase exciton-coupled CD spectrum reappears upon melting of the gel.

Irradiation of the solution and gel samples at 365 nm resulted in isomerization of the azobenzene groups to the *cis* form,^[21] and the disappearance of the CD effect. The *cis* form isomerized thermally (30 °C) back to the *trans* form, with clear differences being observed in the kinetics for the solution and the (*S*)-**1** and (*R*)-**1** gels (Table 2).

The isomerization of (*R*)-**2** in solution followed first-order kinetics. In the gels, however, a deviation from first-order kinetics was observed and the data concur with two simultaneous first-order reactions containing fractions a_s and a_t of a

Table 2. Thermal *cis-trans* isomerization at 30 °C^[a].

Sample	$k_s \times 10^{-5} [\text{s}^{-1}]$	a_s	$k_t \times 10^{-5} [\text{s}^{-1}]$	a_t
(<i>R</i>)- 2 , solution	1.84 ± 0.005	1.0	—	—
(<i>R</i>)- 2 , in (<i>S</i>)- 1 gel	4.6 ± 0.1	0.58	21.9 ± 0.4	0.42
(<i>R</i>)- 2 , in (<i>R</i>)- 1 gel	5.1 ± 0.1	0.59	29.5 ± 0.3	0.41

[a] For an explanation of the symbols, see the text.

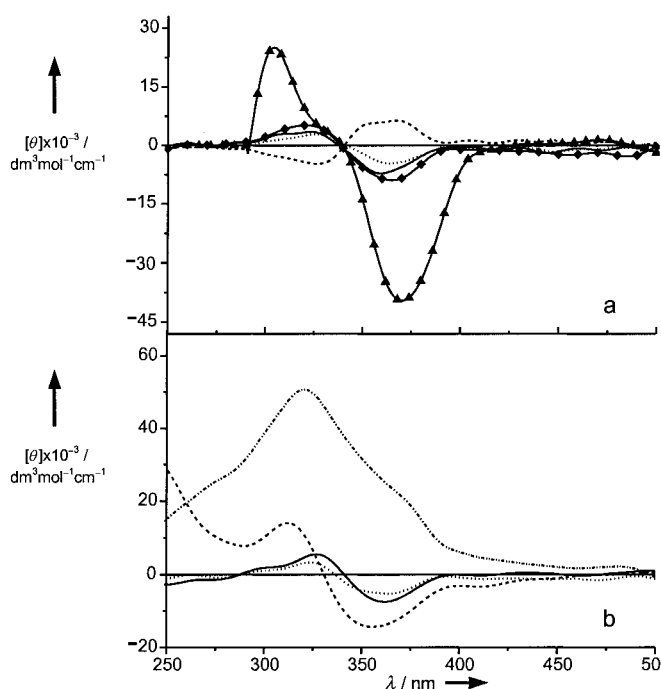


Figure 2. a) CD spectra of solutions of (*R*)-**2** in 1-butanol (—), 1-octanol (—♦—), chloroform (—•••—), and *p*-xylene (—▲—), and (*S*)-**2** in 1-butanol (---). b) CD spectra of (*R*)-**2** in a 1-butanol gel of: (*S*)-**1** at 25 °C (—•••—), (*S*)-**1** at 45 °C (—•••—), (*R*)-**1** at 30 °C (—•—•—), and (*R*)-**1** at 45 °C (—).

slow (k_s) and a fast (k_f) reacting component.^[22] Remarkably, the isomerization was found to be slower in 1-butanol than in the gels. Furthermore, isomerization in the (S)-**1** gel was found to be slower than in the (R)-**1** gel, especially for the fast reacting component. Apparently, the azobenzene groups in (R)-**2** experience a more exposed "solvent-like" environment in the (S)-**1** gel than in the (R)-**1** gel (Scheme 2). These results support the CD measurements, and can be explained by the different packing of **2** in aggregates of the same or opposite configuration leading to a difference in the free volume and polarity experienced by the azobenzene groups (Scheme 2).

Received: July 18, 2000

Revised: November 6, 2000 [Z15483]

- [1] *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfalz, H. Yamamoto), Springer, Berlin, 1999.
- [2] E. L. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, 1994.
- [3] Chiral supramolecular structures: a) M. C. Feiters, R. J. M. Nolte in *Advances in Supramolecular Chemistry, Vol. 6* (Ed.: G. W. Gokel), JAI Press, Stamford, 2000, p. 41, and references therein; monolayers: b) M. V. Stewart, E. M. Arnett, *Topics in Stereochemistry, Vol. 13*, Wiley, New York, 1982, p. 220; c) E. M. Arnett, N. G. Harvey, P. L. Rose, *Acc. Chem. Res.* 1989, 22, 131; liquid crystals: d) F. Stevens, D. J. Dyer, D. M. Walba, *Angew. Chem.* 1996, 108, 955; *Angew. Chem. Int. Ed. Engl.* 1996, 35, 900; e) Y. Takamishi, H. Takezoe, Y. Suzuki, I. Kobayashi, T. Yajima, M. Terada, K. Mikami, *Angew. Chem.* 1999, 111, 2502; *Angew. Chem. Int. Ed.* 1999, 38, 2353.
- [4] Discrete complexes: a) C. D. Tran, J. H. Fendler, *J. Am. Chem. Soc.* 1980, 102, 2923; b) A. Dobashi, N. Saito, Y. Motoyama, S. Hara, *J. Am. Chem. Soc.* 1986, 108, 307; c) S. K. Ghosh, *J. Peptide Res.* 1999, 53, 261; d) G. Castronuovo, V. Elia, A. Pierro, F. Velleca, *Can. J. Chem.* 1999, 77, 1218; e) S. Hanessian, R. Saladino, R. Margarita, M. Simard, *Chem. Eur. J.* 1999, 5, 2169; f) M. Asakawa, H. M. Janssen, E. W. Meijer, D. Pasini, J. F. Stoddart, *Eur. J. Org. Chem.* 1998, 983.
- [5] Micellar aggregates: reviews: a) A. Dobashi, M. Hamada, *J. Chromatogr. A* 1997, 780, 179; b) H. Wan, L. G. Blomberg, *J. Chromatogr. A* 2000, 875, 43; see, for example: c) J. Bella, S. Borocci, G. Mancini, *Langmuir* 1999, 15, 8025.
- [6] Self-assemblies in organic solvents: a) M. T. Cung, M. Marraud, J. Neel, *Biopolymers* 1978, 17, 1149; b) B. S. Jursic, S. I. Goldberg, *J. Org. Chem.* 1992, 57, 7172.
- [7] a) P. Terech, R. G. Weiss, *Chem. Rev.* 1997, 97, 3133; b) J. van Esch, F. S. Schoonbeek, M. de Loos, E. M. Veen, R. M. Kellogg, B. L. Feringa, *NATO ASI Ser. Ser. C* 1999, 527, 233–259; c) J. H. van Esch, B. L. Feringa, *Angew. Chem.* 2000, 112, 2351; *Angew. Chem. Int. Ed.* 2000, 39, 2263.
- [8] a) R. Oda, I. Huc, S. J. Candau, *Angew. Chem.* 1998, 110, 2838; *Angew. Chem. Int. Ed.* 1998, 37, 2689; b) D. J. Abdallah, L. Lu, R. G. Weiss, *Chem. Mater.* 1999, 11, 2907; c) C. Shi, Z. Huang, S. Kilic, J. Xu, R. M. Enick, E. J. Beckman, A. J. Carr, R. E. Melendez, A. D. Hamilton, *Science* 1999, 286, 1540; d) L. A. Cuccia, J.-M. Lehn, J.-C. Homo, M. Schmutz, *Angew. Chem.* 2000, 112, 239; *Angew. Chem. Int. Ed.* 2000, 39, 233; e) U. Beginn, G. Zipp, A. Mourran, P. Walther, M. Möller, *Adv. Mater.* 2000, 12, 513.
- [9] K. Hanabusa, K. Shimura, K. Hirose, M. Kimura, H. Shirai, *Chem. Lett.* 1996, 885.
- [10] a) J. van Esch, S. De Feyter, R. M. Kellogg, F. De Schryver, B. L. Feringa, *Chem. Eur. J.* 1997, 3, 1238; b) J. van Esch, F. Schoonbeek, M. de Loos, H. Kooijman, A. L. Spek, R. M. Kellogg, B. L. Feringa, *Chem. Eur. J.* 1999, 5, 937.
- [11] Bis-ureas (R)-**1**, (S)-**1**, (R)-**2**, and (S)-**2** were prepared by adding the corresponding isocyanate to (R,R)- or (S,S)-1,2-diaminocyclohexane. Bis-urea **1** gels solvents such as *p*-xylene, chloroform, cyclohexane, and butanol; see ref. [10b]. Compound **2** is poorly soluble in solvents such as butanol and *p*-xylene ($c \leq 2$ mM) but gels chloroform and benzene thermoreversibly ($c \leq 4$ mM).
- [12] Measurements were performed at 50 °C, which is above the gel–sol phase transition.
- [13] J.-L. Dimicoli, C. Hélène, *J. Am. Chem. Soc.* 1973, 95, 1063.
- [14] J. Jazdyn, M. Stockhausen, B. Zywicki, *J. Phys. Chem.* 1987, 91, 754.
- [15] M. Akiyama, T. Ohtani, *Spectrochim. Acta Part A* 1994, 50, 325.
- [16] Explanation of the symbols: A = host (R)-**1** or (S)-**1**; D = guest (R)-**2**; c = total urea concentration (M); δ_a = chemical shift of the fully aggregated state; δ_{obs} = observed chemical shift; δ_m = chemical shift of the monomer.
- [17] FT-IR measurements on **2** (CHCl₃; 2 mM) showed a shift of the NH stretch and amide I band from 3435 and 1663 cm⁻¹ for a solution at approximately 50 °C (monomer) to 3322 and 1628 cm⁻¹ for a gel at 20 °C (hydrogen-bonded aggregates), see Y. Mido, *Spectrochim. Acta Part A* 1973, 29, 431. ¹H NMR titration experiments of **2** (CDCl₃; 2–0.5 mM) revealed just a slight change (less than 0.006 ppm).
- [18] It was assumed that as **1** and **2** exhibit the same bis(ureido)cyclohexane skeleton the effect of aggregation on the chemical shift of the NH1 proton of **2** is similar when **2** is incorporated in stacks of **1** as in stacks of pure **2**. It is then possible to treat the chemical shift of **2** (δ_{obs}) as a function of the total concentration (c) of (R)-**2** + **1**, and Equation (1) can be applied. Self-association of **2** is negligible at $c \leq 2$ mM.
- [19] X. Song, J. Perlstein, D. G. Whitten, *J. Am. Chem. Soc.* 1997, 119, 9144.
- [20] N. Harada, K. Nakanishi, *Circular Dichroic Spectroscopy*, University Science Books, Mill Valley, 1983.
- [21] *Photochromism, Molecules and Systems* (Eds.: H. Dürr, H. Bouas, H. Laurent), Elsevier, Amsterdam, 1990.
- [22] C. Ruslim, K. Ichimura, *Macromolecules* 1999, 32, 4254.

Palladium-Catalyzed Domino Reaction of 4-Methoxycarbonyloxy-2-butyne-1-ols with Phenols: A Novel Synthetic Method for Cyclic Carbonates with Recycling of CO₂**

Masahiro Yoshida and Masataka Ihara*

Allylic and propargylic carbonates are well-known compounds that undergo a variety of palladium-catalyzed transformations, which make up an important class of palladium-catalyzed reactions.^[1, 2] The key step in these reactions is the formation of a π -allyl- or -allenylpalladium complex by facile decarboxylation, which undergoes a variety of further transformations under neutral conditions. In these reactions, CO₂ is produced as a co-product in the decarboxylation step, but there are few reports on the recycling of this CO₂ molecule.^[3] Recently, the chemistry of CO₂ has received much attention from the viewpoint of carbon resources and environmental problems,^[4] and the fixation of CO₂ as cyclic carbonates represents an attractive area of organic synthesis.^[5–9] Here we report a novel synthesis of cyclic carbonates by palladium-catalyzed domino reaction of 4-methoxycarbonyloxy-2-butyne-

[*] Prof. M. Ihara, M. Yoshida
Department of Organic Chemistry
Graduate School of Pharmaceutical Sciences
Tohoku University, Aobayama, Sendai, 980-8578 (Japan)
Fax: (+81) 22-217-6877
E-mail: mihara@mail.pharm.tohoku.ac.jp

[**] M.Y. acknowledges support from the Research Fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists.