

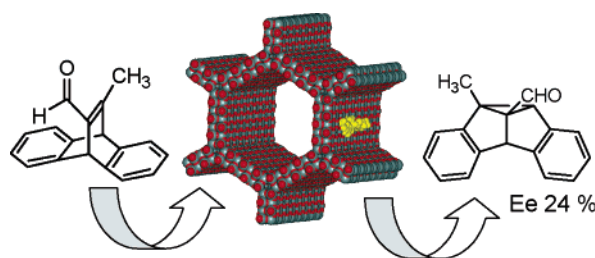
Design of a Chiral Mesoporous Silica and Its Application as a Host for Stereoselective Di- π -methane Rearrangements

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A chiral periodic mesoporous organosilica (ChiMO) was prepared, in which a 1,2-bis-(ureido)-cyclohexyl linker (38 wt %) is introduced into the walls of the hybrid organic–inorganic material. This silica was used as a host for 11-formyl-12-methyldibenzobarrelene (**2**), and the stereoselectivity of the di- π -methane rearrangement of **2** within this host–guest complex was studied. At low conversions, the only product was the corresponding dibenzosemibullvalene. An enantiomeric excess of 24% at 11% conversion was obtained using the ChiMO as host. These values compare well with those achieved using a system based on conventional faujasites (LiY and NaY) as hosts incorporating a chiral auxiliary. We tested *S*-phenylglycine, *S*-proline, *S*-camphanic acid, and *S*-mandelic acid as chiral auxiliaries. In contrast to the behavior of the ChiMO material, adsorption of dibenzobarrelene in purely siliceous mesoporous MCM-41 silica (3.2 nm pore size) containing ephedrine failed, a failure that can be explained as arising from the large internal silanol population and high hydrophilicity of the siliceous MCM-41 sample.

Introduction

Catalytic enantioselective reactions have been one of the major achievements in organic chemistry during the past decades, since the chirality of substoichiometric amounts of a catalysts may lead to a large amount of chiral products producing an effective amplification of chirality present in the catalyst.^{1,2} In contrast to the degree of understanding and the remarkable progress in thermally induced catalytic reactions, the situation in the field of stereoselective photochemical reactions is still far from being satisfactory.^{3,4} The vast majority of known photochemical reactions do not require any catalyst and

apparently in most of the cases studied up to now the interactions between a molecule in its excited state and a chiral auxiliary are generally too weak to promote high enantiomeric excesses.

In this regard, a major achievement in the field of stereoselective photochemical reactions has been the “ionic-auxiliary concept” developed by Scheffer’s group.⁵ According to this concept, the achiral chromophore is connected to a carboxylic acid, and subsequent salt formation with a chiral amine gives chiral salts that crystallize in chiral space groups. The solid-state irradiation of these crystals often results in highly stereoselective transformations. Even though this methodology has been a significant breakthrough in asymmetric photochemistry and the stereoselectivities achieved are generally excellent, it is still desirable to expand this methodology in order to avoid the need for the carboxylic acid

(5) Gamlin, J. N.; Jones, R.; Leibovitch, M.; Patrick, B.; Scheffer, J. R.; Trotter, J. *Acc. Chem. Res.* **1996**, *29*, 203–9.

[†] Instituto de Tecnología Química CSIC-UPV.

[‡] Universität Würzburg.

[§] Universität Siegen.

(1) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008–2022.

(2) Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2024–2032.

(3) Inoue, Y. *Chem. Rev.* **1992**, *92*, 741–770.

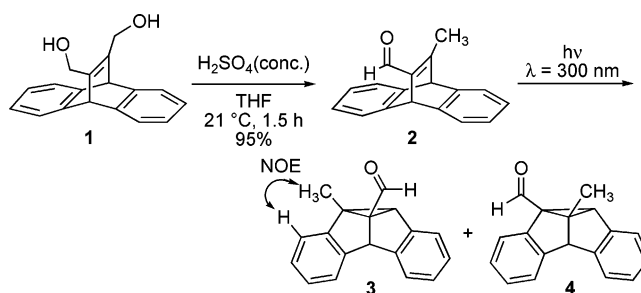
(4) Rau, H. *Chem. Rev.* **1983**, *83*, 535–47.

and amino functionalities and the rather tedious and time-consuming crystallization. In this context, host-guest chemistry has been shown to offer a useful platform if it is possible to use the host molecule to define a confined space in which both a chiral auxiliary and the photoactive system are complexed.^{6–9} Within such host-guest systems, the close proximity of the chiral auxiliary to the reactive center of the chromophore often leads to asymmetric induction and high stereoselectivities. Zeolites are ideal candidates for host materials because of their regular porous microstructure,^{10–12} and because of remarkable previously reported intrazeolite stereoselectivities using this chiral auxiliary approach.^{7–9} Nevertheless, one limitation of zeolites as hosts for stereoselective photochemical reactions is that the size of internal voids in classical zeolites may be too small for the co-inclusion of auxiliary and the chromophore.¹³ Even for the so-called large pore sized zeolites, the diameter of their internal cavities is about 13 Å, with pore openings of 7.4 Å, and it would be desirable to explore the use of porous hosts with larger pore dimensions. Moreover, stepwise co-inclusion of both the chiral auxiliary and substrate could lead to an inhomogeneous distribution of the two components in the zeolite particle, i.e., not every zeolite cage contains both a chiral auxiliary and substrate molecule.

In view of the above considerations, we wished to test mesoporous silicas such as MCM-41, which exhibit significantly larger pore dimensions than zeolites, as hosts.¹⁴ The MCM-41 structure is formed by an array of parallel hexagonal channels whose diameter can be varied by synthesis in the range between 2 and 6 nm. The MCM-41 channels are so periodically arranged that MCM-41 silicas exhibit characteristic XRD even though their walls are constituted by amorphous silica and there is not a repetitive unit cell. It is worth noting that despite the extensive work on the use of zeolites as solid matrixes to perform asymmetric photochemical reactions,^{7–9} the same methodology has, to the best of our knowledge, not yet been applied systematically to mesoporous materials.

Also in this context, an interesting novel type of material worth examining as host for asymmetric photochemical reactions is periodic mesoporous organosilicas (PMOs) in which an organic moiety forms part of the walls of a strictly regular silica structure with pores in the mesopore range (>20 Å).^{15–18} Recently some of us have reported PMO materials with chiral organic moi-

SCHEME 1



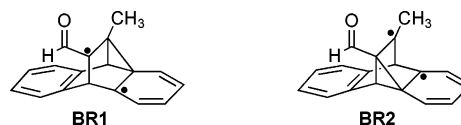
eties (ChiMOs) and observed that they may be used to induce chirality (about ~50% ee) in thermal catalytic reactions.¹⁹ In this paper we compare the conventional NaY zeolite, MCM-41 silica, and a mesoporous ChiMO with chiral organic subunits with respect to their ability to act as host systems for asymmetric photochemical reactions, namely the di- π -methane rearrangement of the dibenzobarrelene derivative **2**.

Results and Discussion

Synthesis and Photochemistry of Dibenzobarrelene 2. We chose dibenzobarrelene **2** as the reference system because it offers the opportunity to investigate the regioselectivity and stereoselectivity of the di- π -methane rearrangement. Thus, irradiation may lead in principle to the dibenzosemibullvalenes **3** and **4**, both of which are chiral (Scheme 1). However, in view of the precedents in dibenzobarrelene photochemistry, it is expected that one of the two possible dibenzobullvalenes (that arising from the most stable biradical) would be preferentially formed over the other.^{20,21}

Dibenzobarrelene **2** was obtained in 95% yield by acid catalyzed rearrangement of the known 11,12-bis(hydroxymethyl)dibenzobarrelene (**1**). Irradiation ($\lambda = 300$ nm) of **2** in acetonitrile gave the semibullvalene **3** with no detectable (¹H NMR) traces of **4**. Semibullvalene **3** was isolated in 61% yield by crystallization. The structural assignment is based on the ¹H and ¹³C NMR data and especially on the detection of an NOE effect between the methyl substituent and the proton at C-1 (see Scheme 1). In compound **4** such an NOE would not be expected. In methanol solution, irradiation of **2** gave the same result; however, prolonged reaction times led to a reduced yield of **3** (as determined by gas chromatography) because of the formation of several unidentified byproducts. In the solid state, the content of **3** in the reaction mixture was also significantly lower (68% before isolation) due to the formation of other unidentified byproducts.

The regiochemistry in the formation of **3** can be explained as arising from the photochemical generation of biradical **BR1** in the initial step of the photoreaction,



i.e., the photoinduced vinyl-benzo bridging.^{20,21} Thus, in

(6) Weiss, R. G.; Ramamurthy, V.; Hammond, G. S. *Acc. Chem. Res.* **1993**, *26*, 530–536.

(7) Leibovitch, M.; Olovsson, G.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1998**, *120*, 12755–12769.

(8) Cheung, E.; Netherton, M. R.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1999**, *121*, 2919–2920.

(9) Chong, K. C. W.; Sivaguru, J.; Shichi, T.; Yoshimi, Y.; Ramamurthy, V.; Scheffer, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 2858–2859.

(10) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401–449.

(11) Scaiano, J. C.; Garcia, H. *Acc. Chem. Res.* **1999**, *32*, 783–793.

(12) Thomas, J. K. *Chem. Rev.* **1993**, *93*, 301–320.

(13) Meier, W. M.; Olson, D. H.; Baerlocher, C. *Zeolites* **1996**, *17*, 1–229.

(14) Garcia, H.; Roth, H. D. *Chem. Rev.* **2002**, *102*, 3947–4008.

(15) Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O. *Nature* **2002**, *416*, 304.

(16) Matos, J. R.; Kruk, M.; Mercuri, L. P.; Jaroniec, M.; Asefa, T.; Coombs, N.; Ozin, G. A.; Kamiyama, T.; Terasaki, O. *Chem. Mater.* **2002**, *14*, 1903.

(17) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867–871.

(18) Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302–3308.

(19) Baleizao, C.; Gigante, B.; Alvaro, M.; Garcia, H.; Corma, A. *J. Catal.* **2004**, *223*, 106–113.

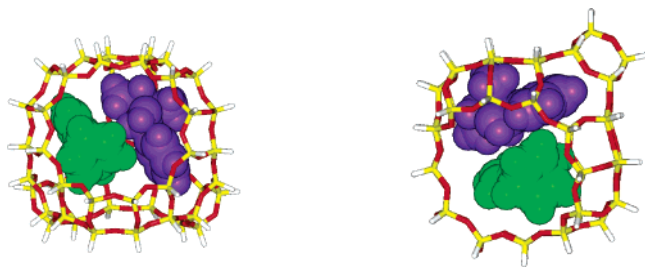


FIGURE 1. Two views of the molecular model showing dibenzobarrelene **2** and *S*-phenylglycine encapsulated within an ideal faujasite supercage devoid of charge-balancing cations. The overlap between the zeolite framework atoms and the organic molecules is not shown for clarity.

biradical **BR1** a formyl-substituted radical center is formed, whereas the alternative pathway leading to compound **4** would require the intermediacy of **BR2**, a less stabilized biradical in which the corresponding radical position is substituted with the comparably less stabilizing methyl substituent.

Adsorption of 2 Within Zeolites and Mesoporous Silica. We next turned to the incorporation of dibenzobarrelene **2** in zeolites and the investigation of the photochemistry of the host–guest systems. For this part of the project, it was necessary to consider that conventional large pore zeolites have a limited void dimension that may be insufficient to include both the substrate and the chiral auxiliary.^{22,23} For instance, NaY faujasite has a pore system formed by almost spherical cages of 13 Å diameter interconnected tetrahedrally through four windows of about 0.74 nm; and the organic guest, the chiral auxiliary, and the charge-balancing cations in order to impart stereoselectivity have to fit within this space.¹³ A molecular model of the dibenzobarrelene derivative **2** and *S*-phenylglycine as chiral inductor encapsulated inside the supercages of faujasite at the AM1 molecular-mechanics level is provided in Figure 1. The model predicts a larger than 20% overlap of the atomic radii that will make co-inclusion of **2** and *S*-phenylglycine in highly crystalline zeolite Y energetically impossible. Situations different from the one corresponding to the molecular model provided in Figure 1 can, however, be envisioned. Thus, it may be that compound **2** and *S*-phenylglycine fit inside incomplete cages at lattice defects or on the external surface or they can interact in other configurations in which the two molecules are not completely inside the same zeolite cavity but protruding throughout the cage windows. In any case, diffusion of the dibenzobarrelene through the faujasite micropores may be significantly hindered by the chiral molecules, which already occupy the binding sites.

The theoretical estimation was confirmed by the adsorption experiments, because a sample of zeolite NaY in which *S*-phenylglycine had previously been adsorbed did not adsorb significant amounts of dibenzobarrelene **2**. Reversing the order of adsorption resulted in a

significant decrease in the amount of coadsorbed *S*-phenylglycine.

We also tested the stepwise coadsorption of a large series of chiral auxiliaries prior to attempting the adsorption of dibenzobarrelene **2**. In addition to *S*-phenylglycine, the list included *S*-proline, *S*-camphanic acid, *S*-phenylalanine, *S*-mandelic acid, *S*-aminophenylpropanol, *S*-phenylglycinol, and *S*-1-phenylethylamine. The amount of adsorbed chiral auxiliary and **2** was determined by weight difference between the initial and the recovered amount. This information was used later to select the most suitable systems to perform asymmetric photochemistry in zeolite. Those cases in which the loadings were too small were not considered further.

In principle the ideal loading of a chiral auxiliary should be at least one molecule per supercage to ensure that each substrate molecule is in the close vicinity of a chiral inductor. Nevertheless, such a high loading cannot be achieved in conventional microporous zeolites. Usually the maximum achievable loading by adsorption is about 25–33% of the total supercages.²⁴

Mesoporous MCM-41 silicas have much larger pore dimensions. The structure of MCM-41 is formed by an array of parallel hexagonal channels.^{25,26} The pore size of the MCM-41 silica sample used in this work has a diameter of 3.2 nm and should be able to accommodate **2** in its interior. Unexpectedly, we were unable to adsorb significant amounts of dibenzobarrelene **2** in an ephedrine-containing MCM-41 sample. Thus, we assume the low degree of adsorption is caused by the characteristic large population of silanol groups on the inner surface of the MCM-41 pores. The resulting hydrophilic internal surface of the pores is unable to adsorb an organic hydrophobic molecule such as **2**. It may happen that the chiral auxiliary having functional groups suitable to form hydrogen bridges could be located at the pore mouth of the MCM-41 channels interacting with the silanols by hydrogen bonds and blocking the access of dibenzobarrelene **2**. Again, this situation is far from the ideal homogeneous distribution of substrate and chiral auxiliary within the internal mesopores.

To circumvent this problem, we investigated a novel type of mesoporous material namely a periodic mesoporous organosilica (PMO) in which the chiral component is covalently linked to the silica framework rather than being coadsorbed in the pores.^{17,27,28} The synthesis of these PMOs is accomplished by adding a suitable chiral disilylalkane to the synthesis gel. Nevertheless, when the organosilane is a large molecule, the synthesis of a PMO requires an additional silicon source. Thus, tetraethyl orthosilicate (TEOS) needs to be added in some proportion to relax the geometrical stress introduced by the bulky organosilane, thus permitting the formation of the PMO structure through co-condensation of the organo-

(24) Corma, A.; Garcia, H. *Eur. J. Inorg. Chem.* **2004**, 1143–1164.

(25) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710–712.

(26) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834–10843.

(27) Inagaki, S.; Guan, S.; Fukushima, T.; Oshuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611–9614.

(28) MacLachlan, M. J.; Asefa, T.; Ozin, G. A. *Chem. Eur. J.* **2000**, *6*, 2507–2511.

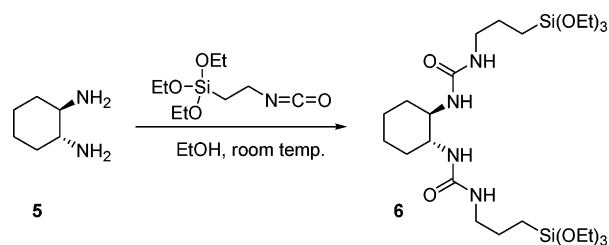
(20) Scheffer, J. R.; Trotter, J.; Gudmundsdottir, A. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song P.-S., Eds.; CRC Press: Boca Raton, FL, 1995; p 204.

(21) Zimmerman, H. E.; Sulzbach, H. M.; Tollefson, M. B. *J. Am. Chem. Soc.* **1993**, *115*, 6548.

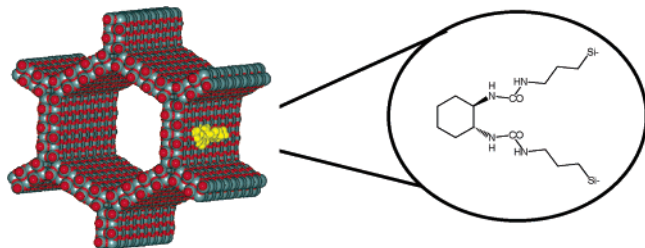
(22) Corma, A.; Garcia, H. *Chem. Commun.* **2004**, 1443–1459.

(23) Davis, M. E. *Acc. Chem. Res.* **1993**, *26*, 111–115.

SCHEME 2



SCHEME 3



silane and TEOS. Preparation of a homogeneous gel ensures a homogeneous distribution of the chiral disilyl-alkane throughout the resulting PMO. This homogeneous distribution has been previously demonstrated in related PMOs by XRD and by high-resolution electron microscopy and it becomes close to the ideal situation in terms of a uniform distribution of the chiral auxiliary through the whole host particle.

Following this synthetic approach, we prepared a CH ∞ -PMO sample in which chiral cyclohexadiyl units (CH) are connected through urea groups to the silica surface within the cavity.²⁹ The required bis(triethoxysilyl)-substituted cyclohexane derivative **6** was obtained by reacting enantiopure *trans*-1*R*,2*S*-1,2-diaminocyclohexane (**5**) with 3-isocyanatopropyltriethoxysilane (Scheme 2). Preparation of CH ∞ -PMO was accomplished with cetyltrimethylammonium (CTA⁺) as the template and chiral cyclohexanediamine derivative **6** and TEOS as the silicon sources. Different solids with varying molar ratios of **6** and TEOS were prepared in order to find the optimum composition, i.e., the one that allows maximal loading of the chiral auxiliary with maintained ordering of a PMO structure. The molar ratios of the components in the precursor gel were 1.00 Si:0.12 CTA⁺:8.0 NH₃ (20%):114 H₂O, where Si corresponds to the total number of silicon atoms from **6** and TEOS. A model of the structure of CH ∞ -PMO material showing the hexagonal channel structure incorporating the cyclohexadiyl units is presented in Scheme 3.

The periodic structure of the resulting PMO with the highest CH loading (CH ∞ -PMO-40 at a weight/weight ratio of **6** to TEOS of 1 to 1) was studied by powder X-ray diffraction analysis, which reveals characteristic peaks of a hexagonal arrangement at 2θ 2° (Figure 2). The crystallinity of the solid is preserved after removal of CTA⁺ by solid–liquid extraction. Isothermal gas adsorption was found to be of type IV according to the IUPAC nomenclature and corresponds to a mesoporous material (Figure 3). Thus, as nitrogen gas adsorption progresses the gas molecules start to cover the solid surface until

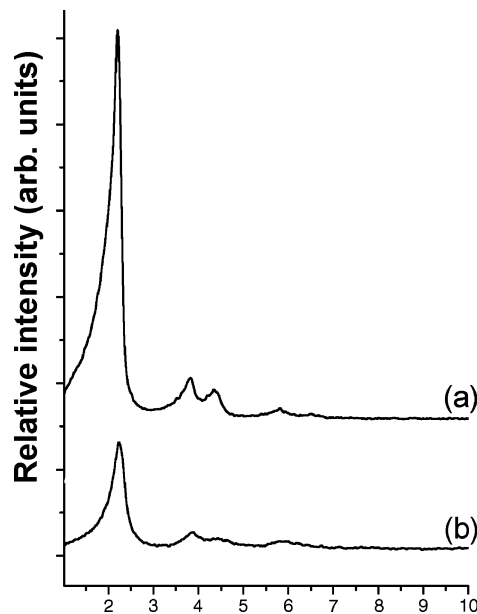


FIGURE 2. Powder XRD patterns of as-synthesized CH ∞ -PMO solids at two different **6**-to-TEOS molar ratios: (a) 5:95 and (b) 20:80.

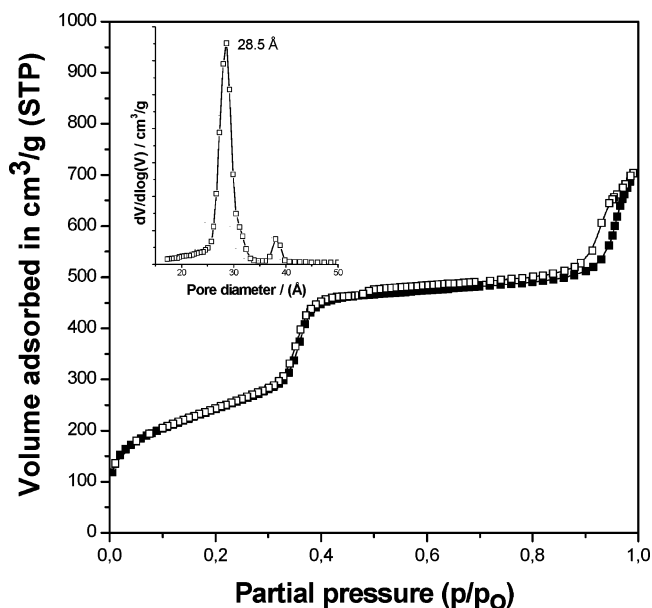


FIGURE 3. N₂ adsorption (■)–desorption (□) isotherms for CH ∞ -PMO (**6**-to-TEOS molar ratio 20:80). The inset shows the pore size distribution for this sample.

at full coverage a monolayer is formed (first part of the plot in Figure 3 up to a relative partial pressure of 0.35). Once a monolayer coverage is reached, a sudden gas adsorption occurs due to the complete filling of the solid mesopores by capillarity (jump occurring in the 0.35–0.4 region of the plot of Figure 3). Beyond this point, further gas uptake corresponds to the filling of solid macropores. Thus, from the plot of Figure 3, the partial pressure at which the sudden gas adsorption occurs is related to the surface area, the verticality of the sudden adsorption indicates a narrow pore size distribution, and the volume of gas uptake in this jump is correlated with the pore volume. By applying the Brunauer–Teller

(29) De Vos, D. E.; Dams, M.; Sels, B. F.; Jacobs, P. A. *Chem. Rev.* **2002**, *102*, 3615–3640.

formalism^{30,31} to the plot of Figure 3, the surface area was estimated to be 878 m² g⁻¹. The pore size distribution gives a diameter of about 2.7 nm as shown in the inset of Figure 3. The CH content was determined by combustion analysis (C and N), whereby it was estimated that 38% of the material by weight corresponds to component **6**, i.e., 75% of the maximum possible CH loading according to the gel composition. To put these characteristics of CH ∞ -PMO into context, the BET surface area of NaY was 410 m² g⁻¹ and typical organic loadings are below 15 wt %.

The integrity of the urea groups was confirmed by the characteristic IR-absorption band corresponding to the urea units (1640 cm⁻¹). The covalent linkage between the terminal silicon atoms of compound **6** and the silicate walls was also proved by solid-state MAS CP{¹H} ²⁹Si NMR spectroscopy, revealing a peak at -66 ppm, which was assigned to the Si atoms connected to the methylene group (=O₃Si-CH₂-) and covalently grafted to the walls. Also, the characteristic Q³ and Q⁴ peaks of MCM-41 (-90 and -100 ppm) corresponding to the Si atoms tri- and tetrapodally connected to the silica walls, respectively, were recorded. By contrast, the ²⁹Si NMR signals of the starting material **6** appeared at ca. -45 ppm, and an upfield shift upon substitution of the ethoxy groups by silyloxy bridges had taken place.³² The physical data of the solid under investigation are consistent with the proposed structure for CH ∞ -PMO, i.e., a typical hexagonal channel system of MCM-41 structure with a large content of chiral component **6** grafted to the walls.

Photoreactivity of 2 Within Zeolites and CH ∞ -PMO. It was investigated in preliminary experiments whether dibenzobarrelene **2** exhibits the same photoreactivity in zeolites as in solution. Thus, several zeolites were loaded with **2** and irradiated as solids. Within the faujasites (M = Li, Na, K) the same product was formed as in solution. Within the acidic dealuminated HY zeolite (Si/Al 14) and mesoporous MCM-41 only very low conversions were observed (<5%). On amorphous silica gel, which was used for comparison, the conversion and the amount of **3** formed were also significantly lower than those within the faujasites.

We then turned to zeolites containing coadsorbed chiral auxiliaries as well as CH ∞ -PMO. Upon irradiation of **2**, which has been co-associated with chiral auxiliaries within faujasites, only low or moderate enantiomeric excesses were obtained as determined by circular dichroism (CD) spectroscopy coupled to HPLC³³ on a Chiracel OD-H phase. HPLC-CD coupling is a powerful analytical tool for the analysis of the enantiomeric ratios of various naturally occurring³⁴ or synthetically derived³⁵ chiral compounds. The online coupling to a CD detector facilitates determination of whether the peaks resolved by

TABLE 1. Photoreactivity of Dibenzobarrelene 2 in Faujasites Containing a Chiral Auxiliary or in CH ∞ -PMO

entry	host	<i>T</i> [°C]	<i>t</i> [min]	conv ^a [%]	ee ^b [%]
1	NaY/S-proline	25	35	20	10
2	NaY/S-proline	25	55	39	8
3	LiY/S-proline	25	15	5	8
4	LiY/S-proline	25	30	>95	4
5	NaY/1-S-camphanic acid	25	15	5	30
6	NaY/1-S-camphanic acid	0	30	9	8
7	NaY/S-mandelic acid	25	30	6	<5
8	CH ∞ -MCM-41	25	65	11	24

^a Conversion determined by GC analysis relative to an internal standard (*n*-dodecane), error $\pm 2\%$ of the given data. ^b Enantiomeric excess determined by HPLC-CD analysis on the chiral stationary phase, error $\pm 5\%$ of the given data.

HPLC on a chiral phase are indeed enantiomeric to each other as evidenced by opposite amplitudes in the CD trace at a given single wavelength and, furthermore, permits unequivocal assignment of the enantiomers by recording full CD spectra in the stop-flow mode. A summary of the conversion and enantiomeric excess of product **3** obtained for the di- π -methane rearrangement of **2** associated with chiral auxiliaries within Y faujasites is given in Table 1. With proline or mandelic acid as the chiral additive, ee values of 4–10% were detected. With 1-S-camphanic acid as coadsorbate in sodium faujasite, an ee of 30% was achieved; however, with increasing conversion (9%), the enantiomeric excess dropped to 8%. Noteworthy was the result observed for chiral CH ∞ -PMO, in which semibullvalene **3** was formed in 24% ee at 11% conversion. These values compared favorably with the results obtained using faujasites as hosts. Note that in the latter case no coadsorbed chiral auxiliary was necessary. Thus, an obvious advantage of CH ∞ -PMO is that solid-liquid extraction only led to the recovery of photoproducts along with unreacted starting material.

Summary

In solution the di- π -methane rearrangement of dibenzobarrelene **2** at room temperature in the presence of chiral auxiliaries does not lead to a measurable enantioselectivity. Low to moderate ee values (up to 30 %) may be obtained by performing this photochemical rearrangement inside the cavities of conventional NaY, but the actual ee depends on the nature of the chiral auxiliary. Moreover, within zeolites, a uniform distribution of chiral auxiliary and coadsorbed substrate is difficult to achieve. In addition, purely siliceous MCM-41, which exhibits larger pore sizes than zeolites, was found inadequate as a host, since it fails to adsorb sufficient amounts of dibenzobarrelene **2**. For better adsorption properties, the use of materials with mesopores having chiral organic units covalently grafted to the silica walls (ChiMOs) appears promising. Although the ideal chiral moiety is still to be found, a simple ChiMO material having chiral cyclohexadiyl units and urea linkers exhibits simultaneously a high adsorption capacity for dibenzobarrelene **2** and the highest ee value at 11% conversion for the photorearrangement under study.

(30) Brunauer, S.; Deming, L. S.; Deming, W. E.; Teller, E. *J. Am. Chem. Soc.* **1940**, *62*, 1723–32.

(31) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309–19.

(32) Shea, K. J.; Loy, D. A. *Acc. Chem. Res.* **2001**, *34*, 707–716.

(33) For method-oriented work on LC-CD coupling, see: Mannschreck, A. *Chirality* **1992**, *4*, 163–169.

(34) For first implementation of LC-CD into phytochemical analysis, see: Bringmann, G.; Messer, K.; Wohlfarth, M.; Kraus, J.; Dumbuya, K.; Rückert, M. *Anal. Chem.* **1999**, *71*, 2678–2686.

(35) For LC-CD analysis of synthetic compounds, see: Mino, T.; Tanaka, Y.; Yabusaki, T.; Okumura, D.; Sakamoto, M.; Fujita, T. *Tetrahedron: Asymmetry* **2003**, *14*, 2503–2506.

Experimental Section

General. NMR: ^1H NMR chemical shifts refer to δ_{TMS} 0.0. ^{13}C NMR chemical shifts refer to solvent signals (CDCl_3 ; $\delta 77.0$). C_q , CH , CH_2 , and CH_3 were determined using the DEPT pulse sequence. Elemental analyses of organic compounds were performed at the University of Würzburg, Institut für Anorganische Chemie. Melting points are uncorrected. Photoreactions were carried out at room temperature using low-pressure mercury lamps ($\lambda_{\text{max}} = 300$ nm) in sealed quartz glassware ($\lambda > 210$ nm). Samples were placed ca. 10 cm in front of the lamp. For solution photoreactions, argon gas was bubbled through the solutions for at least 30 min prior to irradiation to provide oxygen-free solutions. The solution photoreactions were performed in acetonitrile or methanol solutions ($c = 10^{-3}$ – 10^{-2} M), and after removal of the solvent the photolyzate was analyzed by gas chromatography or by ^1H NMR spectroscopy. The mass balance and the conversion were determined relative to dimethyl isophthalate (NMR) or *n*-dodecane (GC) as internal standard. Solid-state photoreactions were carried out by placing the solid sample (30–60 μmol) between quartz-glass slides, which were sealed in argon-flushed polyethylene bags. Each sample was irradiated ($\lambda_{\text{max}} = 300$ nm) at room temperature. The photolyzate was dissolved from the quartz plates with dichloromethane. After evaporation of the solvent the reaction mixture was analyzed by gas chromatography, HPLC, or ^1H NMR spectroscopy. Gas chromatography was conducted with a 5% cross-linked phenylmethylsilicone capillary column, 25 m ($T_{\text{initial}} = 60$ °C, $t_{\text{initial}} = 2$ min, rate 15 °C/min, $T_{\text{final}} = 300$ °C, $t_{\text{final}} = 20$ min). HPLC-CD on a chiral phase: The HPLC system was coupled to a spectropolarimeter with a 5 mm standard flow cell: column, Daicel Chiracel ODH 250 \times 4.6 mm, 5 μm ; eluent, *n*-hexane (90%), 2-propanol (10%), each modified with trifluoroacetic acid (0.05%); flow, 0.5 mL/min; the CD trace was detected at 233 nm, UV at 280 nm.

11-Formyl-12-methyl-9,10-dihydro-9,10-ethenoanthracene (2). At 0 °C, 3.00 mL of concentrated H_2SO_4 was slowly added to a stirred solution of 4.00 g (16.2 mmol) of **1** in 150 mL of THF. The solution containing **1** was stirred for 1 h at 0 °C and for an additional 20 h at 21 °C, and subsequently 150 mL of CH_2Cl_2 and 150 mL of H_2O were added. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 . The combined organic layers were washed with saturated aqueous NaHCO_3 solution, until CO_2 -generation stopped. The organic phase was dried with anhydrous Na_2SO_4 . Removal of the solvent in a vacuum (40 °C, 10 mbar) gave 3.80 mg (15.4 mmol, 95%) of dibenzobarrelene **1** as a white solid, which was crystallized from $\text{MeOH}/\text{CH}_2\text{Cl}_2$ to give white needles, mp 234–236 °C ($\text{MeOH}/\text{CH}_2\text{Cl}_2$). IR (KBr): $\tilde{\nu}$ 1652 cm^{-1} (C=O). UV (CH_3CN): λ_{max} (log ϵ) 210 nm (4.37), 215 (4.36), 273 (3.38), 278 (3.42). ^1H NMR (CDCl_3 , 200 MHz): δ 2.38 (s, 3H, CH_3), 4.96 (s, 1H, CH), 5.78 (s, 1H, CH), 6.99–7.07 (m, 4H, Ar–H), 7.33–7.39 (m, 4H, Ar–H), 9.87 (s, 1H, CHO). ^{13}C NMR (CDCl_3 , 50 MHz): δ 46.9 (CH_3), 59.0 (CH), 59.1 (CH), 123.4 (CH_{ar}), 123.5 (CH_{ar}), 124.8 (CH_{ar}), 125.6 (CH_{ar}), 143.3 (C_q), 143.9 (C_q), 144.8 (C_q), 167.8 (C_q), 185.1 (CHO). MS (70 eV): m/z (%) 246 (37) [M^+], 217 (100) [$\text{M}^+ - \text{CHO}$], 178 (18) [$\text{C}_{14}\text{H}_{10}^+$]. HRMS calcd for $\text{C}_{18}\text{H}_{14}\text{O}$ (M^+) 246.1045, found 246.1046. Anal. for $\text{C}_{18}\text{H}_{14}\text{O}$ (246.30): calcd (%) C 87.78, H 5.73, found (%) C 87.33, H 5.73.

8b-Methyl-8b,8d-dihydro-4bH-dibenzo[*a,f*]cyclopropa[*cd*]pentalene-8c-carbaldehyde (3). Under argon-gas atmosphere, a solution of 70.0 mg (284 μmol) of **2** in 70 mL of CH_3CN was irradiated in a Rayonet photoreactor ($\lambda_{\text{max}} = 300$ nm) for 10 min. The solvent was removed in vacuo (40 °C, 10 mbar) and the remaining yellow solid was crystallized from $\text{MeOH}/\text{CH}_2\text{Cl}_2$ to yield 42.3 mg of dibenzosemibullvalene **3** (172 μmol , 61%) as a white powder, mp 62–63 °C ($\text{MeOH}/\text{CH}_2\text{Cl}_2$). UV (CH_3CN): λ_{max} (log ϵ) 269 nm (4.16), 277 (4.14). ^1H NMR

(CDCl_3 , 200 MHz): δ 1.98 (s, 3H, CH_3), 3.88 (s, 1H, CH), 5.04 (s, 1H, CH), 7.04–7.21 (m, 8H, Ar–H), 9.59 (s, 1H, CHO). NOESY NMR (CDCl_3 , 600 MHz): Cross-peak between 1.98 and aromatic proton at 7.22 (C-1). ^{13}C NMR (CDCl_3 , 50 MHz): 15.9 (CH_3), 50.8 (CH), 51.3 (CH), 52.1 (C_q), 53.6 (C_q), 120.1 (CH_{ar}), 120.3 (CH_{ar}), 122.6 (CH_{ar}), 123.7 (CH_{ar}), 125.4 (CH_{ar}), 125.5 (CH_{ar}), 126.3 (CH_{ar}), 126.5 (CH_{ar}), 134.8 (C_q), 137.5 (C_q), 147.7 (C_q), 149.1 (C_q), 196.0 (CHO). MS (70 eV): m/z (%) 246 (19) [M^+], 217 (100) [$\text{M}^+ - \text{CHO}$], 202 (77) [$\text{M}^+ - \text{CHO}, \text{CH}_3$], 178 (34) [$\text{C}_{14}\text{H}_{10}^+$]. HRMS calcd for $\text{C}_{18}\text{H}_{14}\text{O}$ (M^+) 246.1047, found 246.1041.

Preparation of *N,N*-Bis[3-(trimethoxysilyl)propylamino-carbonyl]-*trans*-(1*R*,2*R*)-(-)-cyclohexdiamine (6). Compound **6** was synthesized by slow addition of a solution of 3-isocyanatepropyltrimethoxysilane in 10 mL of acetonitrile to a solution of 1*R*,2*R*-(-)-1,2-diaminocyclohexane in dry acetonitrile under inert atmosphere. After the addition, the solution is stirred magnetically for 2 h. Compound **6** is obtained by recrystallization from methanol of the residue after acetonitrile removal under reduced pressure. Found combustion analysis (%): C 57.25, H 10.70, N 9.65. Calcd for $\text{C}_{26}\text{H}_{56}\text{N}_4\text{O}_8$ (%): C 56.52, H 10.14, N 10.14.

Preparation of $\text{CH}_x\text{-PMO}$.³⁷ Compound **6** was used in combination with tetraethyl ortosilicate (TEOS) in the synthesis of $\text{CH}_x\text{-PMO}$ and cetyltrimethylammonium bromide (CTABr) as the structure-directing agent. The molar proportions of the components in the precursor gel were 1.0 Si:0.12 CTABr:8.0 NH_3 (20%):114 H_2O .

TEOS and compound **6** were used as a source of Si. Several **6**:TEOS molar ratios were tested, and highly structured materials were obtained below 50:50 weight ratio. After mixing the reactants at 20 °C and stirring the mixture for 2 h the resulting gel was transferred to a polyethylene container and heated at 90 °C for 4 days. The solid obtained was washed with water and dried in air at 60 °C. The structure-directing agent was removed by extracting the solid with dilute ethanolic HCl acid solution at 40 °C for 2 h (20 mL of 0.5 M ethanolic HCl for 0.5 g of solid).

$\text{CH}_x\text{-PMO}$ was first characterized by powder X-ray diffraction (XRD) to test for structure periodicity. XRD patterns were recorded on a Philips X'pert diffractometer using Nickel filtered Cu $\text{K}\alpha$ radiation with $\lambda = 1.54178$ Å operating at 40 kV and 35 mA. Pore size and surface area of the samples were measured by nitrogen adsorption on a Micromeritics ASAP 2010 analyzer. Samples were outgassed at 150 °C for 6 h. Infrared spectra were measured on a Jasco 460 Plus spectrophotometer. Solid-state ^{29}Si MAS NMR spectra were recorded on a Bruker 400 spectrometer with samples packed in zirconia rotors spinning at 5.5 kHz.

General Procedure for Zeolite Loading. (a) Suspension: Prior to the loading of the zeolites, they were heated in an oven to remove water (MY, MX, HY; 20 h at 300 °C; silica gel: 3 h at 120 °C; MCM-41: 15 h at 300 °C; $\text{CH}_x\text{-PMO}$: 20 h at 150 °C). To accommodate dibenzobarrelene **4** or chiral additives within the host systems, 2.40 g of the latter, which was still hot, was added to a solution of 163 μmol of dibenzobarrelene **4** in 80 mL of CH_2Cl_2 or to 163 μmol of the chiral compound in 80 mL of MeOH. The resulting suspension was stirred for 20 h under argon-gas atmosphere at room temperature. The complex was filtered off, washed with dichloromethane (guest: **4**) or methanol (chiral guest), and dried in vacuo (25 °C, 10 mbar). The amount of complexed guest was determined indirectly by gravimetric analysis of the noncomplexed substance in the filtrate.

(b) Ground solid: In a mortar 1.0 g of the activated zeolite was ground thoroughly with 350 μmol of the corresponding guest substance until a homogeneous solid was obtained. The solid was washed with dichloromethane (guest: **4**) or with methanol (chiral guest) and subsequently dried in vacuo. The

(36) Chen, J.; Pokkuluri, P. R.; Scheffer, J. R.; Trotter, J. *Acta Crystallogr. Sect. C* **1993**, *C49*, 2018–19.

(37) Alvaro, M.; Benitez, M.; Debasish D.; Ferrer, B.; Garcia, H. *Chem. Mater.* **2004**, *16*, 2222–2228.

amount of complexed guest was determined indirectly by gravimetric analysis of the noncomplexed substance in the filtrate.

General Procedure for Photolysis of 4 Within Zeolites. The zeolite complexes were distributed on the inner walls of quartz glassware, which were previously wetted with dichloromethane. The flask was then flushed with argon gas for 20 min to remove the solvent and oxygen. The flask was then sealed and irradiated in a Rayonet photoreactor ($\lambda = 350$ nm). After irradiation, the photolyzate was extracted with CH_2Cl_2 (Soxhlet apparatus). The solvent was removed in vacuo and the reaction mixture was analyzed by gas chromatography.

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