Building an Organic Zeolite from a Macrocyclic TADDOL Derivative or How to Teach an Old Dog New Tricks

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Dedicated to Professor *Dieter Seebach*, for his unfaltering and inspiring enthusiasm as a scientist and teacher, on the occasion of his 65th birthday

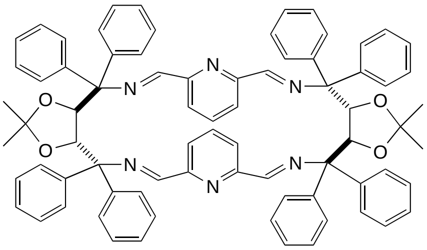
Crystal structures of the macrocyclic TADDOL ($\alpha,\alpha,\alpha',\alpha'$-tetraaryl-1,3-dioxolane-4,5-dimethanol) derivative **A** and its clathrate with diethyl ether are presented. Both the host and clathrate crystallize in the same space group ($P2_12_12_1$) with very similar cell dimensions, *i.e.*, they are isomorphous. At ambient temperature, diethyl ether escapes from **A** · Et_2O, and clathrate single crystals are transformed into the guest-free form without breakdown of the crystal lattice. Conversely, crystalline **A**, when exposed to Et_2O vapor, incorporates guest molecules in a ratio of up to *ca.* 1:1. This behavior, usually the hallmark of inorganic nanoporous materials, allows to describe this compound as an 'organic zeolite'.

1. Introduction. – Porous materials are generally associated with inorganic zeolites, natural as well as synthetic ones [1–3]. These structures are termed *nanoporous* when the cavities are <20 Å in diameter and *mesoporous* with cavities of 20–500 Å. Porous structures are of considerable industrial importance in areas such as shape-selective catalysis, chemical separation based on shape/size effects, and ion-exchange membranes, among others.

In principal, organic materials offer distinct advantages for the scaffolding of a porous host framework. By introducing functional groups, structural diversity can be imposed on the C skeleton to control the target network. The nature and size of cavities can be better controlled by *inter*molecular forces, such as H-bonding or hydrophobic interactions. On the other hand, organic inclusion compounds suffer from a special feature: by definition, zeolites are a class of compounds in which the guest molecules can be removed without the collapse of the host structure. With organic molecules, however, the isotropic nature of intermolecular interactions and, consequently, closest packing, seem insurmountable obstacles for the design of 'organic zeolites' [4]. In spite of these less-than-favorable prospects, the rational design and synthesis of organic porous solids is generally acknowledged as a major challenge in advanced material research [5–7].

A statistical analysis of the organic structures in the *Cambridge Crystallographic Database* (April 1998) revealed that 85% of the crystals are not solvated, despite the fact that practically all substances had been recrystallized [8]. Even with the possibility of relatively strong interactions between solute and solvent, the inclusion compound is usually only stable when *multi-point recognition with strong and weak H-bonds between solvent and solute molecules facilitates the retention of organic solvents in crystals* [8]. Regarding the potential of retaining solvent molecules in the crystal lattice, a distinction has to be made between host structures where the guests are located in closed cavities and those forming channels that allow free passage of solvent. In the latter case, it is common knowledge that, depending on the vapor pressure of the solvent and the number and nature of intermolecular interactions in the solid state, such inclusion crystals tend to lose their 'guests' quite rapidly under concomitant collapse of the crystal structure. Hence, *bona fide* clathrates, by *Powell*'s original definition [9] a kind of trapping rather than binding device, are much rarer than simple solvated crystals. For the attempted design of organic porous materials, however, the formation of this particular class of inclusion compounds is a prerequisite, since facile removal of the guest compound is required.

Organic inclusion compounds [10–12] have found diverse applications in organic chemistry, *e.g.*, in solid-state reactions and resolutions of racemates [13][14]. Various polyfunctional organic molecules have been studied with regard to their properties for building inclusion compounds. Thereby, the so-called TADDOLs (**t**etra**a**ryl**d**ioxolane-**d**imethan**ol**s) have proven very successful in many areas [15]. These molecules had originally been devised as chiral ligands in homogeneous asymmetric catalysis [16]. However, even at an early stage, a marked tendency for the formation of inclusion compounds was recognized during purification, which led, in one case, to the characterization of a TADDOL · CCl_4 clathrate [17]. This property was used later to obtain well-defined, crystalline TADDOL solvates [13][18–20]. In view of their excellent inclusion properties, it is not too surprising that the TADDOL derivative **A** described in this account qualifies as an authentic organic zeolite.



A

2. Solid-State Structures. – The macrocyclic derivative **A** displays a strong tendency of forming inclusion compounds, which was already recognized in the first recrystallization experiments¹). A batch of single crystals was obtained from Et_2O/MeOH. The first attempt to structurally elucidate compound **A** was unsuccessful. The crystals seemed to be quite unstable, because X-ray diffraction measurements, conducted at

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¹) Compound **A** was synthesized and fully characterized in the course of the diploma thesis of *T. Knöpfel* [21] in the group of Prof. *Seebach*.

ambient temperature, failed after several hours due to a pronounced intensity loss[2]. ^{1}H-NMR Measurements of crystals from this batch revealed the presence of *ca.* 1 equiv. of Et_2O. Since the failure of the first measurement was obviously due to loss of the volatile solvent from the crystal lattice, another attempt to solve the crystal structure was made. A new crystal was taken out of the mother liquor, cut to the appropriate size, glued to a glass fiber, and mounted under a N_2 stream at 131 K on a *Nonius Mach3* four-circle diffractometer. The crystal parameters were essentially the same as in the previously attempted room-temperature measurement. Although reflection intensities were uniformly weak, they remained more or less constant over the course of the entire data collection (1 week). The structure was finally solved by direct methods, but the refinement was not satisfactory due to the lack of sufficient reflections and unacceptable atomic displacement parameters. The residual electron density clearly indicated that some unidentified solvent was still present. The difference maps, however, did not permit us to reasonably model the electron density.

In view of the dissatisfying outcome, another attempt to obtain better structural data was made. For weak reflection intensities, as in the present case, the use of an area detector is often beneficial because of the large redundancy associated with this methodology. In addition, data collection is much faster, which is also advantageous when weakly bound solvents are present. Inspection of the crystal mounted on the diffractometer showed that it had remained intact and transparent, although the low-temperature device had been switched off after data collection. Thus, the same crystal was mounted on a *Nonius KappaCCD* diffractometer at room temperature, and data collection was repeated. Surprisingly, this new set of data did not give rise to problems with the residual electron density. Small residual electron density peaks ($+0.82/-0.47$) were found in the solvent-accessible area, but they did not suggest interpretation in terms of a molecular fragment. Because of the large number of non-H-atoms (86) in the asymmetric unit and due to the fact that the crystal had undergone a single-crystal-to-single-crystal transformation, the noise present in the refinement was just below the residual electron density peaks in the cavity. An ORTEP drawing of the molecular structure of **A** in the solid state is shown in *Fig. 1*.

Taken together, these findings pointed to the presence of an organic host framework including solvent molecules and, most intriguingly, showing loss of guest molecules while retaining the crystal integrity. In other words, such a behavior is that of a true zeolite. To unequivocally prove the identity of the crystal lattice in both cases and to determine the exact location of the trapped ether molecules, another measurement of the clathrate was mandatory. A crystal from a later crystallization batch was taken out of the mother liquor, mounted by the oil-drop technique, and measured on the *KappaCCD* diffractometer at 193 K. This time, after refinement of the host component, the difference map showed 10 peaks easily interpretable as two Et_2O molecules. Refining the two positions, fixing the total occupancy at 1, led to acceptable results. The behavior of the atomic-displacement parameters indicated further possible orientations of the solvent molecules in addition to the two found in the difference maps. Thus, several models with up to 4 different geometries for every atom of Et_2O were refined,

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[2] These measurements were carried out by Prof. *V. Gramlich* on a *Picker-Stoe* four-circle diffractometer at the Laboratorium für Kristallographie, ETH Zürich.

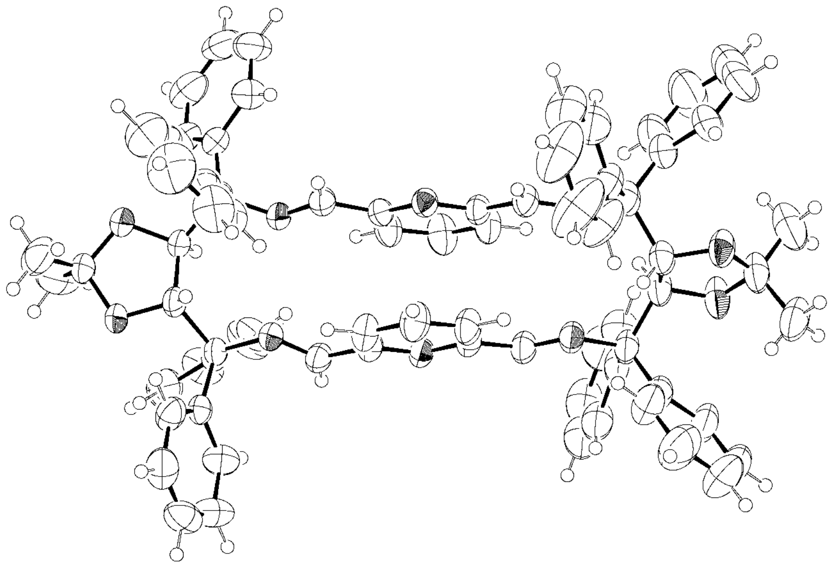

Fig. 1. *ORTEP Drawing of the structure of* **A** *in the solid state.* Thermal ellipsoids are shown at 50% probability.

but this did not result in a physically more-meaningful picture. The present model with only two positions is, thus, a compromise between simplicity and flatness of the difference map.

The coordinates obtained from this processing were used as a starting point in the refinement of the first data set collected on the *Mach3* diffractometer. Even so, the refinement proved rather unsatisfactory due to the lack of a sufficient number of observed reflections. The *R* value dropped to *ca.* 6%, which clearly indicated that the structure of the two crystals was basically the same.

To confirm that essentially no solvent had remained in the crystal lattice after keeping the first crystal for two weeks at room temperature, the structure model of **A** · Et_2O was used in a complementary refinement of the data set obtained on the *KappaCCD* at ambient temperature. The occupancy parameter of the solvent molecules was refined to see whether or not the difference map would improve with at least partial presence of Et_2O. This refinement converged at an occupancy of *ca.* 0.1, without flattening of the difference map. As had been shown previously by NMR (see *Exper. Part*), the crystals still contained Et_2O (<0.1 equiv.), even after drying for several hours *in vacuo*. Thus, the presence of some residual Et_2O is not unexpected. Obviously, it is not possible to distinguish between signals generated by 1/10 of a C-atom and some noise always present in a refinement.

The structure of **A** in the solid state (*Fig. 1*), basically consists of two building blocks: the bulky heads of the TADDOL-derived part (TADDAMIN, [22]) and the spacer in between. The spacer is composed of two almost coplanar pyridyl units. The angle between the two least-squares planes of the pyridine rings is *ca.* 4° in the structure of **A** and *ca.* 5° in the corresponding ether clathrate. The mean distances between these planes and the center of the adjacent pyridine rings are 3.24 Å in **A** and 3.21 Å in

A · Et_2O. Superimposition of both structures shows only very slight differences in the orientation of the phenyl rings (maximum deviation: 0.26 Å). Thus, the sole significant difference between the two structures is, indeed, the presence or absence of the solvent molecules.

With regard to the arrangement of the Et_2O molecules in the unit cell, the common *fishbone* motif can be identified when one looks down the *b*-axis. As the molecules are somewhat narrower in the central part, the formation of the lattice by stacking the macrocycles on top of each other generates voids that can be occupied by smaller guests. As can be seen from *Fig. 2*, channels run through the crystal lattice along the *b*-axis. Additional channels are also formed along the *a*-axis, but these are tightened by phenyl rings of neighboring molecules (*Fig. 3*). In other words, the solvent-accessible areas are arranged as crossed channels along the axes *a* and *b*, allowing free passage of guest molecules in both directions.

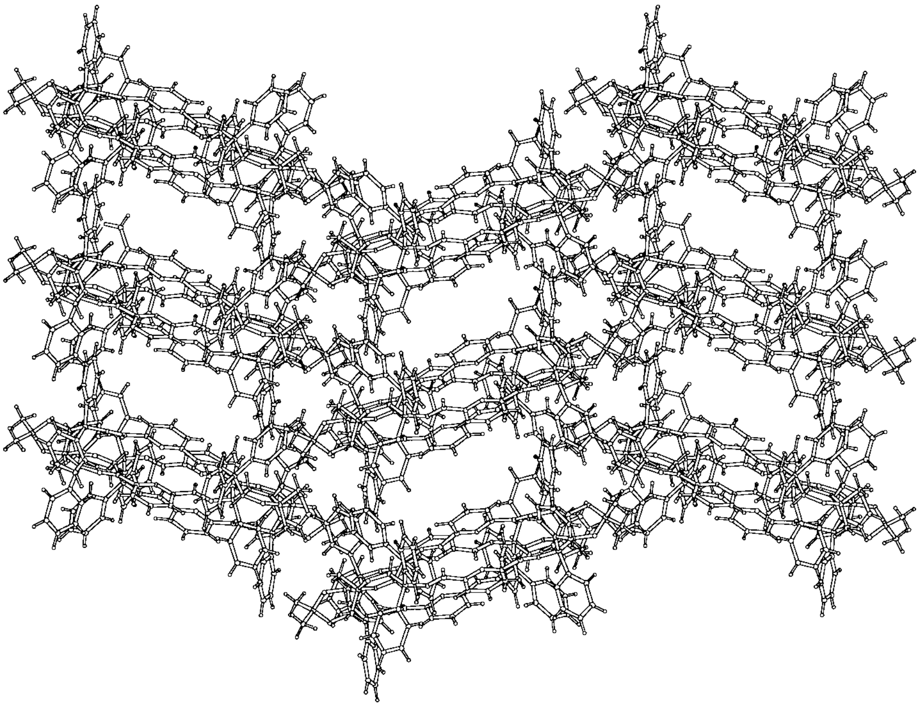

Fig. 2. *'Ball-and-Stick' Presentation of the crystal packing of* **A** *viewed along the* b-*axis*

It may be assumed that the rigid pyridyl spacer between the TADDAMIN head-groups is one key element that allows the lattice to remain stable while solvent molecules move in and out. It is interesting to note that the intermolecular contacts are solely made up by hydrophobic interactions between the bulky head parts; not a single H-bond is present in the whole structure. The solvent-accessible volume of plain **A** calculated with the *PLATON* program [23] amounts to *ca.* 1300 $Å^3$ per unit-cell (18% of the cell volume) and is made up by two cavities of 645 $Å^3$ each.

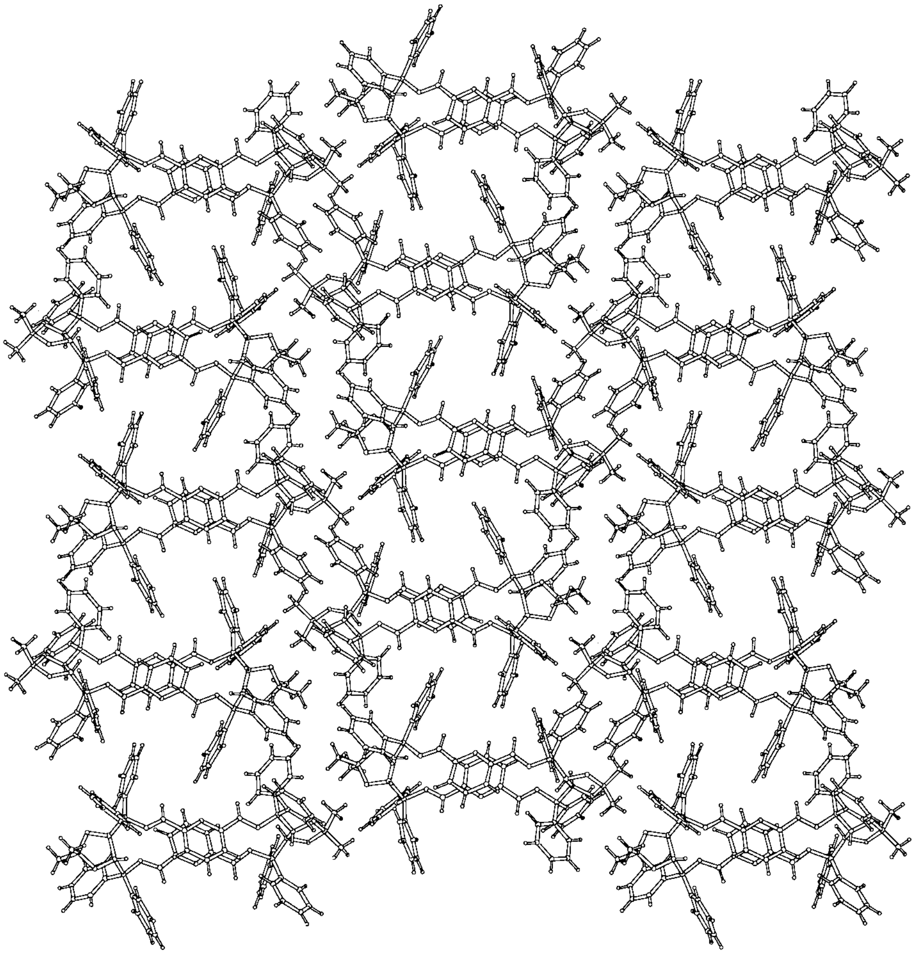

Fig. 3. *'Ball-and-Stick' Presentation of the crystal packing of* **A** *viewed along the* a*-axis*

Two perspectives of the crystal packing of the host/guest structure of **A** $\cdot$ Et_2O are shown in *Fig. 4*. Considering that, statistically, only one of the two solvent positions is occupied on average, it is no surprise that a revised calculation, with only one position of the solvent molecule filled in, still suggests the presence of solvent-accessible areas. However, the NMR experiment and the crystallographic data strongly suggest the presence of only 1 equiv. of Et_2O. Also, refinement of the structure with 2 equiv. of Et_2O led to considerable positive and negative peaks in the difference maps.

3. Sorption Experiments. – Given that single crystals of **A** $\cdot$ Et_2O do lose their guest molecules without collapsing, to be qualified as an authentic 'organic zeolite', it remained to be demonstrated that the reverse pathway, *i.e.*, incorporation of Et_2O, into the crystal lattice, can take place as well. Since the solubility of **A** in Et_2O hampered soaking experiments in the liquid phase, a sample of finely powdered **A** was exposed to

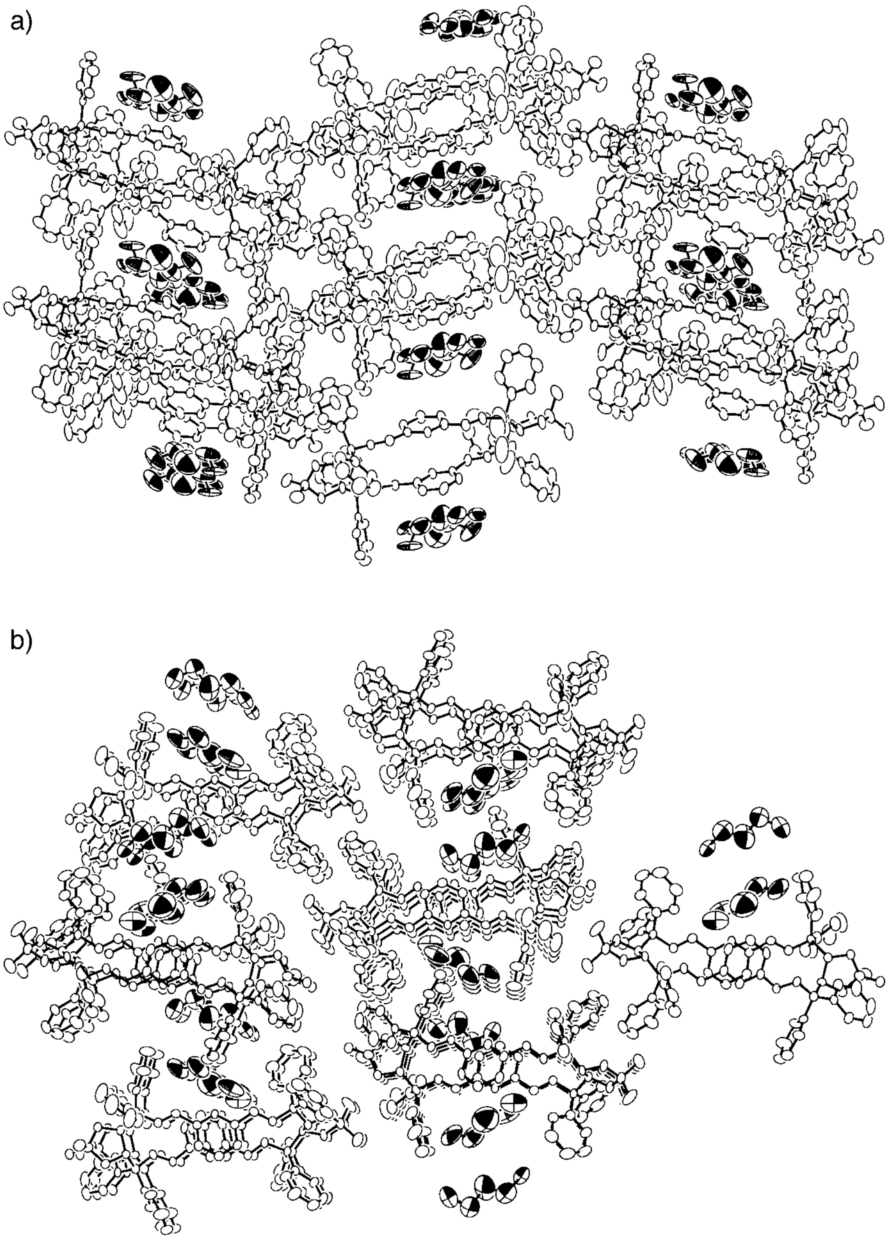

Fig. 4. a) *ORTEP Representation of the crystal structure of* **A** · *Et_2O along the* b-*axis.* b) *ORTEP Representation of the crystal structure of* **A** · *Et_2O along the* a-*axis.* Both positions of the included Et_2O are shown. For clarity, H-atoms have been omitted, and different representations of host and guest ellipsoids have been chosen.

Et_2O vapor, as described in the *Exper. Part*. The result of this sorption experiment is shown in *Fig. 5*. The graph shows a sharp decline in Et_2O content within the first 2 h after removing the sample from the Et_2O atmosphere. We interpret this finding as evaporation of the physisorbed Et_2O molecules from the surface of **A**. From this point on, the graph is characterized by a much slower and constant decrease, which can be interpreted in terms of Et_2O release from the crystalline host/guest framework. As known from ^1H-NMR studies of **A** recrystallized from Et_2O/MeOH, the maximum uptake of Et_2O is one equivalent [21]. Extrapolating the slow decay backwards leads to a value somewhat lower than one, which can be explained by the fact that inclusion from the gas phase into a pre-existing crystal lattice can never be as efficient as compared to crystal formation in solution. In view of the fact that the exposure time to Et_2O vapor was, inevitably, finite, the performance of **A** as an organic compound capable of reversibly binding guest molecules in a zeolitic manner is impressive.

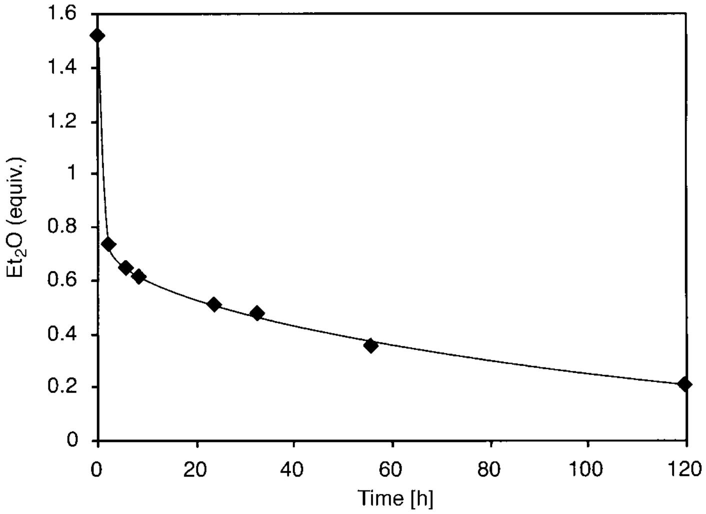

Fig. 5. *Drop-off diagram of the room-temperature Et_2O content in crystalline* **A** *with time*. For the determination of the experimental values plotted, see the *Exper. Part*.

4. Discussion. – The design and synthesis of porous materials beyond the classical inorganic zeolites has become a major challenge in modern material sciences. The rational design and scaffolding of *open-framework* structures is generally achieved by the exploitation of directed intermolecular interactions. In what is often called '*organic zeolites*', such intermolecular forces are usually coordinative interactions between organic building blocks and metal ions [24]. In a purely organic context, *i.e.*, disregarding proteins, polymers, and organometallics, host/guest inclusion compounds come into play. The analogy between host/guest solid-state structures and zeolites has often been stressed [5][7][10–12]. However, the crystalline form of such 'hosts' is usually not known or drastically different³). This behavior rules them out for being

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³) For a survey of inclusion compounds, see the following article in this issue [25].

classified as *organic zeolites*, for which the following properties are mandatory: *1*) the host has to retain its cavities upon removal of the guest, *2*) reversible absorption and desorption of the guest, must be possible, and *3*) guest molecules must be bound selectively [5]. Adhering strictly to this definition, those borderline cases where organic inclusion compounds tend to rapidly exchange their guests, while maintaining their structural integrity, must also be dismissed [26].

The purely organic, porous structure of **A** fulfills the criteria stated above exactly. It represents an open-framework structure in the sense that 'open' implies *allowing passage as in open door or window* [27]. In practically all other cases of organic host/guest solid-state structures that particular property is absent, because the guest molecules, even when occupying channel-like cavities, cannot be removed without compromising the integrity of the crystal structure. One of the few examples of an organic zeolite, the classic case so to speak, is *Dianin*'s 4-(*p*-hydroxyphenyl)-2,2,4-trimethylchroman [28]. This compound retains its solid-state cage structure upon removal of the guest species (e.g. noble gases, CO_2, simple alkanes, alcohols *etc.*) [29]. It has early been recognized that hexameric units of chroman host molecules, linked by a network of H-bonds, are stacked on top of each other, thus, leaving cages between the assemblies [30]. Since H-bonds constitute the strongest intermolecular interactions, it is not surprising that H-bridged frameworks often constitute the basic structural motif in other examples of purely organic, nanoporous structures [31][32]. An exhaustive literature search has shown that, in any case, the total number of organic isomorphous one- and two-component crystal structures is very small [25]. Only one of these resembles the structure of **A** in that the inclusion compound of octakis(*m*-tolylthio)naphthalene and its 'empty' form are lacking stabilization by strong intermolecular forces, the frameworks being held together only by hydrophobic interactions [33]. However, since the included 1,4-dioxane molecules reside in closed compartments, this system does not qualify as an authentic organic zeolite according to the above definition.

In view of the observation that the framework formed by the TADDOL derivative **A** in the solid state is held together by weak forces, the question remains why it remains stable upon loss of the guest molecules. We assume that key elements for the stability include the neat interlocking of the phenyl substituents of neighboring molecules, as well as the rigidity of the pyridyl moieties. However, we can, by no means, claim that the determined structure of solvent-free **A** is the only stable crystal phase. Our attempts to crystallize **A** from different solvents, or even without solvents, have by no means been exhaustive. Thus, the question whether or not **A** might crystallize in a polymorphous, possibly denser form, remains open.

5. Conclusions. – The crystal structure of **A** includes *for some structural reasons* [...] *vacant spaces* in the solid state that are suited to accommodate guest molecules [34]. To the best of our knowledge [25], this system constitutes the only case of a solid, purely organic compound held together by hydrophobic interactions and where the guests can be removed reversibly while the crystal lattice remains intact. This behavior demonstrates that the vacant spaces are *in the form of open channels providing ingress and egress* [34]. The present system is, therefore, a prototype of a hydrophobic scaffold suited for the design of organic materials with zeolite properties. Much more experimental work is required, though, to arrive at a quantitative theory for clathrate formation – a prerequisite for crystal engineering to develop into a practical form of 'supramolecular synthesis' [35]. In view of the structural and functional diversity of organic compounds, which should permit unique tailor-made material properties, such a rational crystal engineering would be certainly highly desirable.

Synthesis of **A** by *T. Knöpfel* is gratefully acknowledged[1]). For assistance in the sorption experiment, the authors would like to thank *Lukas Gehrer* and *Claudio Bomio*. Finally, we are indebted to Prof. *V. Gramlich* for preliminary X-ray diffraction experiments.

Experimental Part

General. Solvents: Et$_2$O and MeOH were purchased in *p.a.* quality from *Fluka*. ^{1}H-NMR: *Varian Mercury-XL-300* (300 MHz) spectrometer, chemical shifts δ in ppm with Me$_4$Si (δ 0 ppm) as internal standard.

Sorption Experiment. The macrocyclic TADDOL derivative **A** was dried *in vacuo* (0.01 Torr) at 80° for several hours, until the ^{1}H-NMR spectrum displayed only traces of Et$_2$O (*ca.* 0.02 equiv.). A desiccator (21 cm diameter) was equipped with a crystallizing dish (8 cm) filled with *ca.* 140 ml of Et$_2$O. A modest vacuum was applied until the Et$_2$O started to boil gently.

The desiccator was disconnected, and, after a few min, the procedure was repeated. After that, the desiccator was opened, the crystallizing dish refilled with Et$_2$O, and a petri dish (9.5 cm), covered with *ca.* 100 mg of finely-dispersed crystalline **A**, was placed in the desiccator. This sample was kept in the desiccator for several days, during which time vacuum was applied in the above described fashion once every day. Condensation of Et$_2$O on the walls of the desiccator between the evacuation procedures was taken as a sign for

Table. *Data for the X-Ray Analyses of* **A** *and* **A** $\cdot$ *Et$_2$O*

	A	**A** $\cdot$ Et$_2$O
Formula	$C_{76}H_{66}N_6O_4$	$C_{76}H_{66}N_6O_4 \cdot C_4H_{10}O$
Mol. weight	1127.40	1201.52
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a [Å]	10.2815(2)	10.4014(17)
b [Å]	20.1734(4)	20.196(3)
c [Å]	34.0728(5)	33.757(7)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
Volume [Å^3]	7067.1	7091.2
Z	4	4
$F(000)$	2384	2552
ρ [g cm^{-3}]	1.060	1.125
μ [mm^{-1}]	0.066	0.070
Crystal size [mm]	0.10 × 0.20 × 0.25	0.17 × 0.23 × 0.29
T [K]	293	193
Radiation	MoK_α ($\lambda = 0.7107$)	MoK_α ($\lambda = 0.7107$)
θ_{max} [°]	25.02	22.50
Reflections measured	61505	20325
Independent reflections	11311	8715
Reflections in refinement	9022	6468
Number of variables	776	866
R (final)	0.0581	0.0616
R_w (final)	0.0542	0.0643
Weighting scheme	3 parameters[a])	5 parameters[a])
max/min in difference map	0.82/ – 0.47	0.81/ – 0.46

[a]) *Chebychev* polynomial [41].

the saturation of the etheral atmosphere. After 12 d, the dish was removed from the desiccator, and a first sample was taken for ^{1}H-NMR measurements. The dish was then equipped with a cover glass and kept on the bench at r.t. After 2, 5.5, 8.5 h *etc.* (see *Fig. 5*), additional samples were taken for NMR measurements. For the determination of the Et_2O loading of the crystals, the integrals of the signals for the two methine protons (*s* at 4.85 ppm) and of eight selected aromatic protons (*m* at 7.67 – 7.71 ppm) of **A**, respectively, were weighed against the Et_2O methylene protons, and the average value was taken thereof. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.25 (*s*, 2 Me); 0.94 (*s*, 2 Me); 1.20 (*t*, 2 OCH_2*Me*); 3.47 (*q*, 2 OCH_2Me); 4.85 (*s*, 2 CH), 6.32 (*s*, 2 CH); 7.05 – 7.25 (*m*, 16 arom. H, 2 HC = N); 7.38 – 7.50 (*m*, 22 arom. H); 7.67 – 7.71 (*m*, 8 arom. H); 8.20 (*s*, 2 HC = N).

X-Ray Crystal-Structure Determination. Details of the structure determination of both **A** and **A** · Et_2O are compiled in the *Table*. Crystals were mounted on a *Nonius KappaCCD* diffractometer. Data collection and integration were carried out with the *Nonius* collect suite [36]. The structures were solved by direct methods using the program SIR92 [37]. The absolute configuration of the methine C-atoms was assigned all-(*S*), since the synthesis of **A** involved (*S,S*)-TADDAMIN [22]. Least squares refinements were carried out with the program CRYSTALS [38]. The graphic plots were produced with the programs MacMoMo [39] and Ortep3 for Windows [40]. *Chebychev* polynomial weights [41] were used to complete the refinement. Crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition Nos. CCDC-186881 and CCDC-186882.

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