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Synthesis of Shape-Persistent Macrocycles with Three 1,8-Diazaanthracene Units and Their Packing in the Single Crystal

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Abstract: The synthesis of four shapepersistent macrocycles with three 1,8diazaanthracene units each is reported (2,3a-3c). For two of them single crystals could be obtained and the structures in the crystal be solved. The structures reveal that macrocycle 2 self-dimerizes in the solid state; surprisingly it also forms a stable dimer in solution. The reason for this is seen in unusually efficient dispersion interac-

Keywords: crystal packing · macrocycles · shape-persistence · supramolecular self-dimerization

tions as a consequence of the large contact areas in the dimer. All macrocycles are assessed as to their applicability in lateral polymerizations in the single crystal as well as in solution.

Introduction

Anthracenes (A)^[1] and their heteroaromatic aza^[2] and diaza analogues^[3] are important photochemically active units. Light-induced dimerization via [4+4]-cycloaddition has been studied in great detail particularly for homoaromatic anthracenes and used for the creation of complex compounds^[1,4] and polymers^[5] derived from simple components presenting one or more of these units. Substituted As tend to furnish anti dimers and aza-, as well as diazaanthracenes (DAA), have an even stronger anti-preference.^[2b,3,6] Recently, we have started a program aiming at exploring shape-persistent macrocyclic compounds^[7] with two or three A or DAA units for their ability to give polymers by photochemical treatment, both in the solid state and at the air/water interface. This led to the first two-dimensional polymer (2DP),^[8] that is, a covalent monolayer sheet polymer with topologically planar repeat units,^[9] and also a covalent monolayer sheet, the internal structure of which still needs to be proven.^[10] The 2DP and the monolayer sheets were obtained by irradiating a single crystal and a tight monomer assembly at the air/water interface, respectively. While in the 2DP case the A units of neighboring monomers were not face-to-face (ftf) stacked, which resulted in a [4+2]-cycloaddition between the A of one monomer and the acetylene of another, in the sheet case it is assumed that the As are connected via [4+4]-cycloaddition. We also polymerized the shape-persis-

tent $C_{2\nu}$ -symmetric macrocycle **1** with two DAA units towards a rigid rod polymer by photo-irradiation in the single crystal,^[11] whereby the DAA units were in fact packed antiparallel *ftf* resulting in a [4+4]-cycloaddition polymerization. Encouraged by these results, we decided to make available a collection of DAA-based monomers and to investigate in depth their potential in context with the synthesis of 2DP and their congeners, covalent monolayer sheets. These monomers may also be of interest for novel types of doublestranded hyperbranched polymers.^[12]

Here we report a first important step into this matter, the synthesis of compounds 2 and 3a-c which all carry three DAAs and thus potentially qualify as monomers for lateral polymerization in a single crystal (2,3a,3b), at an air/water interface (3a) or in homogeneous solution (3c). We also describe first crystallization studies which in the case of compounds 2 and 3a led to single crystals, the structures of which could be solved by XRD. As will be shown, both structures are not yet suited for 2D polymerization but provide valuable hints how to change crystallization to eventually arrive at a useful packing. The crystal packing of 2 is of interest in its very own right in that this compound forms a homo-dimer reminiscent of the commonly encountered heterodimeric supramolecular aggregates derived from, for example, molecular tweezers and clips.^[13] Because of the scarce availability of supramolecular homo-dimers^[14] the stability of the dimer of 2 was explored towards disassembly in solution by NMR, UV/Vis, and fluorescence spectroscopy at concentrations as low as 10^{-6} M and found to be virtually negligible. The dimer was further investigated by MALDI-ICR mass spectrometry and found to withstand also those conditions. To find a reason for this surprisingly high stability, the electrostatic surface potentials (ESP) of the two residues of the dimer were calculated by the semi-empirical methods AM1 and PM3.^[15] This led us to conclude that the manifold dispersion interactions between the aromatic substructures tightly *ftf* packed within the dimer sum up to a re-

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spectable value which together with an efficient dipol moment compensation results in a stable dimer. Any substantial compensation of ESP, which is often encountered in tweezers and clips, can be ruled out as driving force in this case. Finally, compounds 3a-c will be briefly discussed in terms of their applicability for lateral polymerizations where particularly 3a but also 3c are believed to have a great potential (Figure 1). scale. The overall yield was 7% which is considered reasonable given the complexity of the macrocycle.^[16] Macrocycle **2** and compounds **5b**, **5c**, **5d** were purified by recycling (r)-GPC, compound **7a** by silica gel column chromatography and compound **7b** by easy filtration and washing.

Synthesis of macrocycles **3a–c** is delineated in Schemes 2 and 3. The bridging building blocks **12** and **13** were synthesized from the known 3-bromo-5-iodo-toluene (**8**).^[17] The



Figure 1. Chemical structures of compounds synthesized in this study. Macrocycle 1 has two 1,8-diazaanthracene (DAA) units while macrocycles 2 and 3a-c have three. Compound 2 is shown in two representations. The letters refer to NMR signal assignment in Figures 2 and 4. The assignment of macrocycle 1 follows that of 2.

Synthesis of macrocycles 2 and 3a-3c: Synthesis of compound 2 (Scheme 1) started from the previously reported building blocks dibromo-DAA 4, bridge 5a, and cyclization precursor 6.^[11] Mono substitution of 5a with tri(isopropylsilyl)acetylene (TIPSA) afforded 5b, and further substitution with tri(methylsilyl)acetylene (TMSA) afforded 5c. TIPS and TMS-protected component 5c was then converted into 5d by selective removal of the TMS group in aqueous KOH. Next, precursor 7b was prepared by a twofold intermolecular Sonogashira coupling between 4 and 5d leading to 7a, followed by TIPS removal. In the final step, the two complementary precursors 6 and 7b were cyclized in a 1:1 stoichiometry in a dilute DMF solution (0.2 mM). This procedure furnished macrocycle 2 on a rather useful 100 mg halogens was used for the selective Sonogashira coupling with TIPSA. The remaining bromide was further reacted with bis(pinacolato)diboron under palladium catalysis to give 10. Double Suzuki coupling of 9 with 3,5dibromobenzyl alcohol^[17] afforded 11. This reaction was particularly easy to perform and gave compound 11 in quantities of up to 50 g. Complete desilvlation of 11 with tetrabutylammonium fluoride (TBAF) resulted in 12, while the monodesilylation of 11 with TBAF in a 1.15:1 stoichiometry afforded 13 after purification. All compounds were purified by silica gel column chromatography.

different reactivity of its two

Synthesis of macrocycle **3a** started from the DAA derivative **4** which was coupled either with the terphenylene bridging unit **12** to give **14** or with unit **13** to furnish **15**. Deprotection of **15** to give macrocycle precursor **16** had to be performed at 0°C to avoid black insoluble precipitate which most likely was the product of an uncontrolled oligomerization of deprotected acetylenes. The two precursors **14** and **16** were cy-

clized in diluted solution (2.0 mM) using a 1:1 stoichiometry furnishing macrocycle **3a** on a 600 mg scale (total yield: 5% from **4** and **8**) starting from more than a gram of both **14** and **16**.

Macrocycle **3a** served as starting material for capped derivative **3b** and the alkyl-chain decorated derivate **3c**. Unfortunately, the capping procedure with trimesoyl chloride, turned out to be extremely low yielding and also poorly reproducible. Nevertheless a few mg of this material could be obtained (estimated total yield: <1%) and its existence proven by NMR spectroscopy (Figure 2) and high resolution MALDI ICR mass spectrometry (see below). The esterification of **3a** with *n*-dodecanoyl chloride went much better and afforded the expected macrocycle **3c** reliably on a 70–75 mg



Scheme 1. Synthesis of macrocycle 2 with conditions.

scale (total yield: 2% from **4** and **8**). The ¹H and ¹³C NMR spectra of all compounds are provided in Figures S1–S17.

Macrocycles **3a–c** were analyzed by HR-MALDI ICR mass spectrometry and ¹H and ¹³C NMR spectroscopy. The mass spectra gave the molecular ions $[M+H^+]$ of **3a**, **3b** and **3c** at m/z 1579.6187 (calcd: 1579.6208), 1736.6094 (calcd: 1736.6088) and 2126.1233 (calcd: 2126.1220), respectively. In addition, both ¹H and ¹³C NMR spectra show the expected (small) set of signals in accordance with molecular symmetry. Figure 2 compares the ¹H NMR spectra. The signals of the benzylic hydrogen atoms (*e*) shift from δ = 4.85 ppm in **3a** to δ =5.65 ppm in **3b** and to δ =5.04 ppm in

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3c which reflects the incorporation of an aromatic ester cap and aliphatic ester chains, respectively. Other characteristic signals include the methyl group at $\delta \approx 2 \text{ ppm}$ for all three compounds and the aromatic hydrogens (g) of the cap in 3b. More assignments are given in Figure 2. Note that there is no indication of homodimer formation. The UV/Vis spectra of macrocycles 3a-c have the typical $\pi - \pi^*$ absorptions of the DAA unit at $\lambda =$ 380-480 nm similar to other anthracenes (Figure S18).

Single crystal X-ray structures of macrocycle 2 and 3a: Cubic crystals of 2 were grown by slow liquid diffusion of supernatant toluene into a chloroform solution (Figure 3a). For this purpose a necked vial was used the bottom part of which was filled up to the neck with the chloroform solution before the upper part was charged with toluene. This macrocycle crystallizes in a rectangular conformation (Figure 3b) and, unexpectedly, two such macrocycles mutually penetrate each other to give a homodimer (Figure 3c). The representation in Figure 3b and c and the color code (red and grey) should facilitate understanding the dimer structure. Note that the DAA units in both residues of such a dimer pair are oriented parallel to one another but in opposite direction. The DAA units of one monomer are posi-

tioned at close distance to the bridging units of the other monomer and vice versa. Figure 3d shows two views of the resulting two stacks of DAA (residue1), bridge (residue2), DAA (residue1), and bridge (residue2) units contained in each dimer. For clarity, all other parts of the molecular structures are removed. The distances between neighboring units are well below 4 Å which suggests effective stacking interactions. For a discussion of the driving forces for dimer formation, see below. Interestingly the dimers are arranged into straight arrays (Figure 3e) whereby stacking interactions are again operative. This time it is the pyridine moieties contained in the bridging units which are oriented anti-

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Scheme 2. Synthesis of terphenylene bridging units 12 and 13 with conditions.



Scheme 3. Synthesis of macrocycles 3a-c with conditions.

parallel to one another at a distance of approximately 3.8 Å (Figure 3 f).

Cubic crystals of macrocycle 3a were grown from CHCl₃ (Figure 3). The macrocycles fold-up resulting in two of their DAA units to give a somewhat off-set *ftf* dimer. The remaining DAA unit is involved in an intermolecular *ftf*-stacking with its counterpart of the neighboring macrocycle. Stacking is again off-set and next neighbors are turned upside down. Figure 3 i gives typical distances in these *ftf*-stackings.

Discussion

The single crystals of 2 and 3a show a highly interesting packing of the macrocyles in the crystal lattice, which is, however, unfavorable for any photochemically induced polymerization. Macrocycle 2 forms intimate dimers which are interesting in their own right but, even though there are surprising cases of innercrystal mobility,^[18] it is safe to assume that irradiation of crystals of 2 will not result in 2D polymers. However, as stacking enhances p orbital overlap, the dimer crystals may be interesting candidates to explore, for example, directed charge carrier mobility.^[19] For **3a** at best one may achieve a dimerization of the DAA pairs between neighboring compounds. Despite the off-set within these pairs, the distances of both DAA units (Figure 4c, bottom) are still within the range for topochemical reactions, as first described by Schmidt.^[20] Regarding macrocycle 3b it is noted that although only a very small amount of this compound was synthesized, crystals could be grown (Figure S19). Unfortunately, they contained too many defects for structure determination. Thus, despite its rather promising design,^[8] **3b** is not a useful monomer for polymerization studies unless the synthetic difficulties with introducing the cap and with crystallization can be overcome. It is noteworthy that the packing of both monomers 2 and 3a while being rather different seems to be driven by the same desire namely to prevent the cycles' interior voids from being "empty". Both the homo-dimer of 2 and the tightly selffolded 3a have virtually no residual void. We believe that this interpretation provides the key to eventually rendering these macrocycles into successful monomers. One can well imagine that, if offered an attractive guest for their voids, the macrocycles would co-crystallize as 1:1 host/guest complexes presenting their DAA units in a fixed geometry with 120° between the DAAs. This could then very well result in lavered packing with these complexes being arranged alternatingly up and down and all their DAA units being ftf stacked. Experiments in this direction are on-going. It may

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Figure 2. ¹H NMR spectra of macrocycles **3a** in [D₆]DMSO at 370 K (a), **3b** in [D₂]TCE (tetrachloroethane) at 350 K (b) and 3c in $[D_6]$ -benzene at 338 K (c). Signal assignment refers to Figure 1.

also be of interest to raise the question why macrocycle 2 forms a dimer and 3a does not. The main structural difference between these two compounds are i) the ethanylene bridges connecting the three phenylene units in the heteroterphenylene units of 2 and ii) the hetero-terphenylene bridge in 2 containing a *para*-methoxyphenylpyridyl fragment. While the ethanylene bridges effectively coplanarize the terphenylene units and thus render ftf stacking between them and the next neighbor's DAA units energetically more favorable, the pyridyl fragment significantly adds to compound's 2 overall dipole moment which is effectively compensated in the dimer, the two residues of which are stacked antiparallel. It is thus understandable that 2 has a higher propensity to self-dimerize than **3a**.

Finally, monomer 3a is an attractive candidate for interfacial polymerization. It is amphiphilic and should either be directly spreadable at an air/water interface or after its three hydroxyl groups have been converted into short ethyleneoxy substituents.^[21] Monomer 3c finally is fully soluble even in highly concentrated benzene solution which is the pre-requisite for a successful polymerization into the corresponding double-stranded hyperbranched polymer. Such hyperbranched polymers are unique because of their structure-enforced tendency to assume ellipsoidally flattened coils in solution.[22]

We shall now discuss qualitative experimental studies aiming at determining the stability of dimer 2 towards deaggregation and computational studies aiming at understanding the reasons for its stability. Figure 4a depicts the ¹H NMR spectrum of **1**, which is the lower homologue of **2** and therefore contains only two instead of three repeat units. From its simplicity and the $C_{2\nu}$ symmetry of **1**, it is concluded that this spectrum refers to an individual compound rather than a dimer. Also there is no indication for dimer formation of 1 in the crystal.^[11] Thus, macrocycle 1 in solution oscillates fast on the NMR timescale between iden-

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tical rhombic conformations, and also in the solid state it assumes similar collapsed conformations to prevent the void and maximize stacking interactions.

sharp contrast, In the ¹H NMR spectrum of **2** in [D₂]TCE solution at room temperature is astoundingly complex (Figure 4b), rendering an assignment practically impossible, and the complexity remains basically unchanged even if the temperature is raised from 298 to 383 K. This suggests that macrocycle 2 forms a rather stable supramolecular complex whereby the symmetry is broken and (unresolved) dynamic effects cause line broadening. Given the fact that this

macrocycle in the crystal forms a dimer, we assume that the same applies to the solution, however, the dimer's geometric parameters now being somewhat flexible. The NMR spectra remained unchanged even if solutions with concentrations down to 10^{-3} M were recorded. Remarkably, the signal of the methoxy hydrogen atoms e is the one least affected by this complexation, suggesting that it is furthest away from the central part of the dimer. The lower concentration range was explored by UV/Vis and fluorescence spectroscopy. Figure S20 shows the UV/Vis spectra of 2 at concentrations of 10^{-3} , 10^{-4} and 10^{-5} M in chloroform and Figure S21 displays the corresponding fluorescence spectra in the concentration range from 10^{-3} – 10^{-6} M. Neither of these spectra shows any significant concentration dependence. Thus, if there is equilibrium between monomer and dimer, it is entirely on the dimer side. We further substantiated this aspect by high resolution MALDI-ICR mass spectrometry of a sample in which macrocycle 2 was prepared with DCTB matrix. The spectrum showed the dimer molecular ion at m/z 3765.3877 (calcd for $C_{270}H_{174}N_{18}O_6 [M+H]^+$: 3765.4015) (Figure S22) which is noteworthy because of the long dwelling time in ICR mass spectrometry between ionization and detection favoring disassembly.

The interaction between aromatic components has been studied in quite some detail.^[23] Electrostatic and dispersive forces are the main sources of this interaction. To find out what the driving force for dimer formation was the electrostatic potential surfaces of macrocyles 1, 2 and diethynylsubstituted DAA derivative 17 and bridging unit 18 (the two potential aromatic binding sites of 1 and 2) were calculated by the semi-empirical methods AM1 and PM3.^[15] The molecular structures were also optimized by these methods (Figure S23). The EPS calculations were helpful for the understanding and explanation why various aromatic host molecules such as cyclophanes or molecular tweezers bind preferentially positively charged guest molecules.^[13,24] Contrary

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Figure 3. Single crystal of macrocycle 2: a) Optical microscopy image of crystal habit. b)–f) Packing in the crystal: b) Approach of two macrocycles (red and grey) to illustrate dimer formation. Arrows indicate the opposite orientations of DAA moieties. c) Self-assembled dimer. d) Two views of truncated dimer to show the packing of the DAA units of one macrocycle with the bridging units of the other in the same dimer. e) Top view of the 1D array of dimers. f) Side view of the truncated 1D array to illustrate packing of the dimer bridging units. Solvent molecules are disordered and crystallographically not resolved. Single crystal of macrocycle **3a**: g) Optical microscopy image of crystal habitus. h)–j) Packing in the crystal: h),j) Two different perspectives tilted by 90° of two neighboring macrocycles showing that two of the DAA units of each compound are intramolecularly *ftf*-stacked while one DAA unit of each macrocycle form an intermolecular *ftf* stacking. Both stackings are somewhat off-set i) which prevents [4+4]-cycloadditions across the 9,10-positions (up: intermolecular).

to these host-guest systems, where, for example, the tweezers' arene units show a profoundly negative EPS complementary to the positive guest EPS, the EPS of both aromatic binding sites of macrocycle 1 and 2 is negative, that of the large number of tight contacts between the two residues of the dimer obviously sums up to considerable overall interaction energy. Compounds **3a** and **3c** are promising monomers for interfacial polymerization at the air/water interface and

DAA unit slightly less negative than that of the aromatic bridging unit (Figure S23). Thus, there is no obvious attractive electrostatic interaction between these two units in the dimer of **2**. However, in these extended aromatic systems multiple dispersive interactions are certainly the dominating noncovalent binding force which binds the two molecules together.

Conclusion

In summary, four different macrocycles with three DAA units each, 2 and 3a-c, were synthesized. For two of them, 2 and **3a**, single crystals were grown and the structure be solved by XRD. While these crystals in their present form are not suitable for photochemically induced solid-state polymerization, co-crystallization seems a promising way to nevertheless achieve this goal. The crystals of 2 revealed an unexpected tendency of this macrocycle towards self-assembly into a homodimer. The propensity of the dimer towards disaggregation in solution was investigated at elevated temperature and at concentrations as low as 10⁻⁶ M and found to be negligible. The dimer was stable under all applied conditions including in the MALDI ICR mass spectrometer which sets it apart from other supramolecular dimers, which involve CHaryl,^[25] aryl-aryl^[26] and H-bonding^[27] interactions and are less stable towards dissociation. Electrostatic potential surface calculations suggest that dispersion interactions are the responsible factor behind this stability whereby the unusually



Figure 4. ¹H NMR spectra of macrocycles **1** (a) and **2** at 298 K (b) and 383 K (c) in $[D_2]$ TCE. (Internal standard: $\delta_{\text{TCE}} = 6$ ppm). For signal assignment, see Figure 1.

solution polymerization towards novel hyperbranched polymers, respectively.

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Macrocycles -

Synthesis of Shape-Persistent Macrocycles with Three 1,8-Diazaanthracene Units and Their Packing in the Single Crystal



The perfect fit: Two shape-persistent macrocycles such as **A** form a self-assembled dimer in the single crystal which even under forcing conditions in solution cannot be made to dissociate into the single components.