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Synthesis and Structural Characterization of New Stiff Rod Oligomeric Domains by X-ray Crystallography and NMR

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Received May 28, 2002

The monomers *N*,*N*′-dibenzylbenzene-1,4-diamine **(1)**, *N*,*N*′-dibenzylnaphthalene-1,5-diamine (**2**), and *N*,*N*′-dibenzylanthracene-1,9-diamine (**3**) were reacted with phosgene in the presence of a base to produce the corresponding *N*,*N*′-dibenzyl-1,4-bis(chlorocarbonylamino)benzene (**4**), *N*,*N*′-dibenzyl-1,5-bis(chlorocarbonylamino)naphthalene (**5**), and *N*,*N*′-dibenzyl-9,10-bis(chlorocarbonylamino)-anthracene (**6**). These monomers were used to create zigzag type stacks, in a stepwise fashion, of trimers and 9-mers of either 1,4-diureidobenzenes (**^{Phe}K(3)** and **^{Phe}K(9)**) or 1,5-diureidonaphthalenes (**^{Nap}K(3)** and **^{Nap}K(9)**). A byproduct in the formation of **^{Phe}K(9)** was a cyclic hexamer **^{Phe}K(6)**. NMR gave evidence of the structure in solution while X-ray crystallographic information was obtained for **5**, **6**, **^{Nap}K(3)**, and the cyclic **^{Phe}K(6)**.

Introduction

N-Methylation of benzanilides and *N*,*N*′-diarylureas has a dramatic effect on their structure, as shown first by Yamaguchi and Matsumura.[1] Amides and ureas almost invariably have a flat transoid structure when the nitrogen atoms still have one hydrogen atom attached. Substitution with a methyl group changes the geometry to a cisoid form with the aryl groups placed almost face-to-face.

This characteristic structural feature, called a molecular splint, or the *N*-methyl amide effect, has been exploited to direct the structure of compounds such as calixarenes[2] and metal-binding receptors.[3]

Yamaguchi and Matsumura used the effect to construct a stiff rod of five benzene rings joined in a zigzag fashion by *N*,*N*′-dimethylurea moieties. Their brief and purely structural note inspired us to undertake a further synthetic and structural exploration of this phenomenon. Our motivation was that such rod-like compounds with a central stack type aromatic structure might find several interesting applications. From a purely structural view they could be utilized as a new type of building block to construct very large molecules from domains. The central aromatic moieties have geometry reminiscent of the pancake-like discotic phases of, e.g., electronically conducting alkyl phthalocyanines.[4]

Results and Discussion

From the considerations above several questions immediately came to mind. Could the overall structural features be maintained with other *N*-alkyl groups? And what would happen if the central benzene groups were substituted for larger groups such as naphthalene and anthracene? We chose to use *N*-benzyl groups instead of the *N*-methyl groups to demonstrate that the effect on the structure was maintained but more importantly to create an easy route to large amounts of the monomer units with either a central 1,4-phenyl or 1,5-naphthyl unit (see Scheme 1).

For easy reference to these compounds we have in this paper chosen a new shorthand nomenclature. The whole class of compounds we call K domains (from one of the authors). A prefix (Phe or Nap) designates the central aromatic unit being either a benzene or a naphthalene. A number in parentheses denotes the number of subunits. Thus **^{Phe}K(9)** is meant to identify the 9-mer of 1,4-dibenzylphenylene diamine units joined via urea linkages.

The corresponding diamines were condensed with benzaldehyde to the diimines, which could be reduced quantitatively with sodium borohydride in tetrahydrofuran-acetic acid to *N*,*N*′-dibenzylamines. 1,4-dibenzylaminobenzene (**1**) and 1,5-dibenzylamino-naphthalene (**2**) have been prepared previously from the corresponding diamines and benzyl alcohol.[5] The monomer 9,10-dibenzylaminoanthracene (**3**) was less easily obtained in pure form since it oxidizes readily. Anthraquinone was reacted with formamide at reflux for several hours to prepare 9,10-diformylaminoanthracene as described by Schiedt.[6] This compound could be *N*-alkylated with benzyl chloride and potassium *tert*-butoxide in tetrahydrofuran to produce the rather insoluble *N*,*N*-dibenzyl-9,10-diformylaminoanthracene. Hydrolysis in ethanol with a large excess of potassium hydroxide gave the monomer 9,10-

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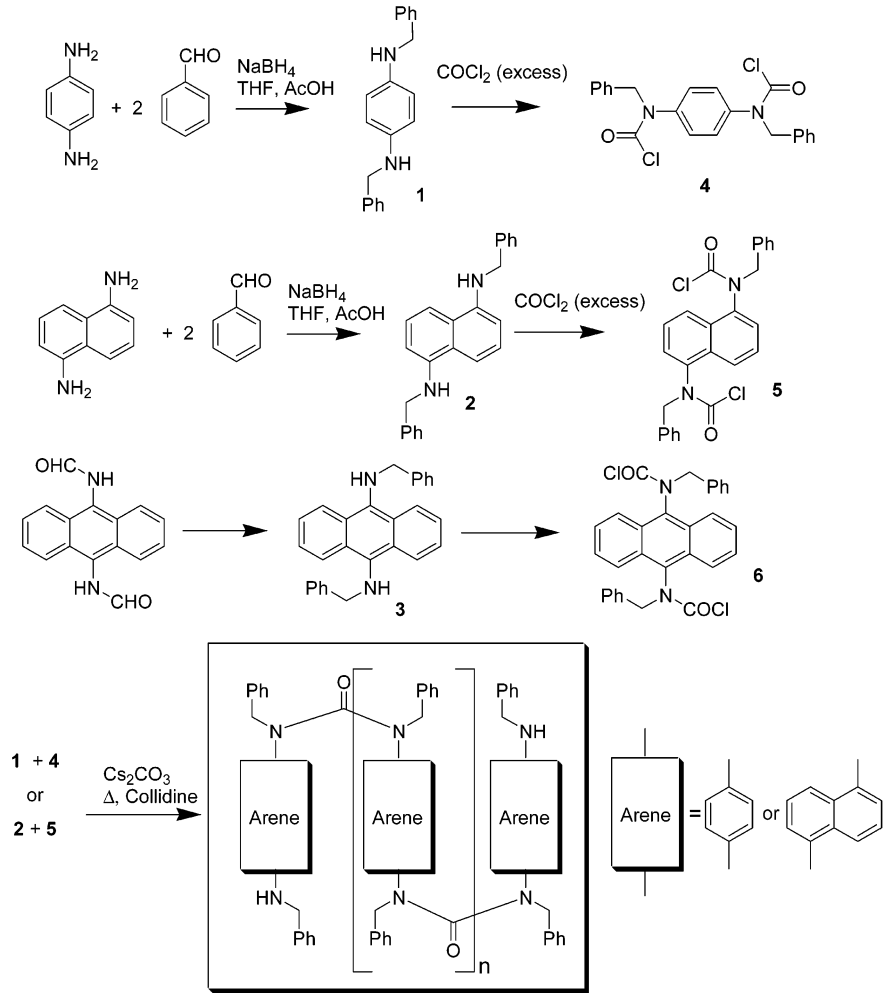
10.1021/jo025980f CCC: $22.00
Published on Web 09/26/2002

SCHEME 1. Synthesis of Monomer Units and Oligomerization Reactions to the ^{Phe}K and ^{Nap}K Oligomer Domains



dibenzylaminoanthracene in low yield. Bis-carbamoyl chlorides (**4**, **5**, and **6**) were then prepared from the three dibenzylamine monomers by reaction with phosgene.

The bis-carbamoyl chlorides could either be isolated as stable crystalline solids or alternatively reacted in situ with an excess of the *N*,*N*′dibenzylamine. It was found that this reaction was rather sluggish at the usual conditions for a reaction between an acid chloride and an amine. Much effort was spent in determining the best reaction conditions. We found that reaction between the bis-carbamoyl chlorides and amines was best carried out in freshly purified collidine (2,4,6-trimethylpyridine) at reflux using dry cesium carbonate as the base. Other combinations of solvents and bases gave poorer yields and a significant amount of decomposition. Thus, pure trimers of the phenyl and naphthalene could be obtained in large scale (50−100 g) after suitable workup (see Figure 2). In the case of the anthracene monomer no trimer could be obtained in our hands. Even prolonged reaction times did not yield any of the desired products.

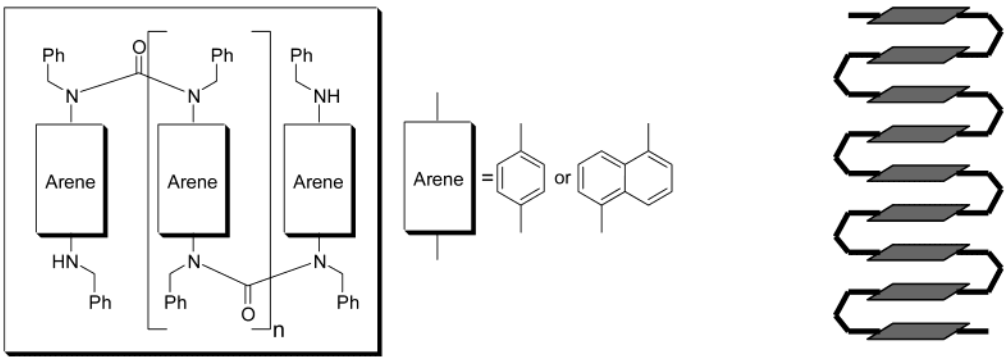


FIGURE 1. Oligomeric aryl-ureido stiff rod domains. On the right is shown a schematic view of the relatively easily prepared 9-mer showing the zigzag type structure with good $\pi-\pi$ overlap of the central aromatic residues.

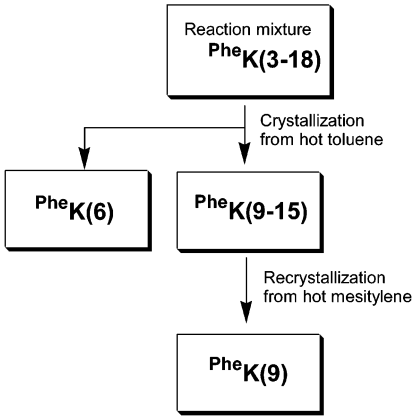


FIGURE 2. Simplified scheme of the workup of a reaction mixture from a reaction between **^{Phe}K(3)** and the corresponding bis-carbamoyl chloride. A cyclic hexamer **^{Phe}K(6)** could be obtained from the hexane washings of the toluene fraction. A pure sample of the less soluble **^{Phe}K(9)** oligomer could be obtained from mesitylene. The same procedure can be used in the naphthalene series where **^{Nap}K(9)** is obtained by repeated crystallization from much mesitylene. A difference is that a cyclic 6-mer is not produced in the naphthalene series.

This is probably due to the instability of the 9,10-dibenzylaminoanthracene that leads to extensive decomposition. Thus we conclude that larger central aromatic moieties than phenyl and naphthyl are not feasible with the present route.

In the phenylene and the naphthylene series of oligomers further extension of the trimers could be carried out by first reaction with phosgene to introduce the carbamoyl groups at each end of the trimers then reaction with excess trimer in collidine with cesium carbonate, at reflux for extended periods of time. The extent of the reaction and the composition of oligomers varied slowly with time and could be conveniently followed by size exclusion chromatography (SEC). Using this approach it was possible to obtain mixtures of oligomers where, e.g., the 9-mers predominated. Pure fractions could be obtained by preparative SEC. This however was not an appealing option since it was our intention to obtain large enough amounts of the substances for growing crystals of X-ray crystallographic quality and for further synthetic elaboration. Instead a fractionated crystallization scheme was developed that gave gram scale quantities of the oligomers in reasonably pure form (see Figure 2). The purity was checked both by SEC and also by a mass spectroscopic technique for large molecules (MALDI-TOF).

A typical oligomerization of the **^{Nap}K(3)** compound to produce the 9-mer can be illustrated from the mass-spectroscopic data obtained from MALDI-TOF shown in Figure 3. A mixture of possible oligomers is formed progressing toward higher molecular mass with time. A sample was drawn and analyzed to give peaks belonging to oligomers **^{Nap}K(3)** to **^{Nap}K(15)**. The trimer can be seen to dominate (MW 1067.32) with the desired 9-mer as the second major component (assuming similar ionization cross sections for the different oligomers). The above-mentioned purification procedure then produced the compound giving the MALDI-TOF spectrum shown in Figure 3 (right) having peaks at 3254 and 3357 (*m*/*z*) which can be ascribed to the 9-mer and a complex with silver ion added to the matrix.

In Solution. Some information on the structure of these compounds in solution can be obtained from their NMR spectra. When aromatic rings are placed in close proximity with fixed orientations dramatic shielding effects can be observed in the ^{1}H spectra. Protons that are placed above the ring plane of an aromatic nucleus will thus have a signal that is shifted toward higher field while the opposite is observed for protons in the aromatic plane. Comparison of the ^{1}H spectra of **^{Phe}K(3)** and **^{Phe}K(9)** with reference compounds 1,4-dibenzylaminobenzene (**1**) and *N*,*N*′-diacetyl-1,4-dibenzylaminobenzene shows that the protons attached to the central 1,4-diaminobenzene rings of **^{Phe}K(3)** and **^{Phe}K(9)** are indeed shifted from about 7.0 ppm to about 6.15 and 6.0−6.3 ppm, respectively. This shift is in accordance with the zigzag type structure shown in Figure 1. The benzylic methylene groups show resonances at ca. 4.0 and 4.5−4.8 ppm. The first group is assigned to the two benzyl groups at the ends of the molecules while the other is assigned to the benzyl groups in the urea linkages. A smaller upfield shifting of these resonances is also observed.

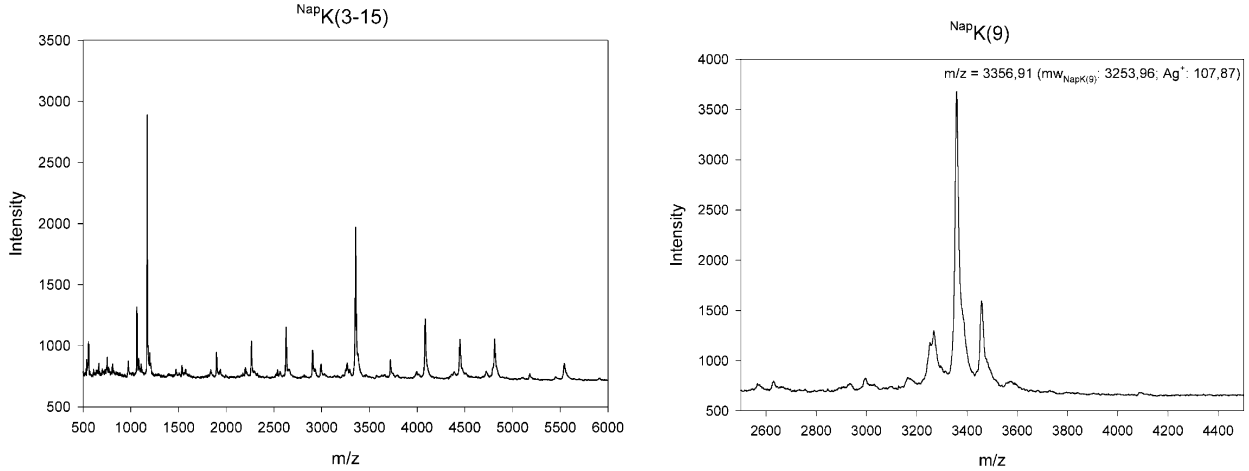


FIGURE 3. Mass spectra (MALDI-TOF) of the crude mixture of oligomers from the synthesis of **^{Nap}K(9)** on the left and the purified 9-mer on the right. Silver triflate was added to the matrix facilitating ionization so most peaks are due to a molecular ion + Ag (107.87 g/mol).

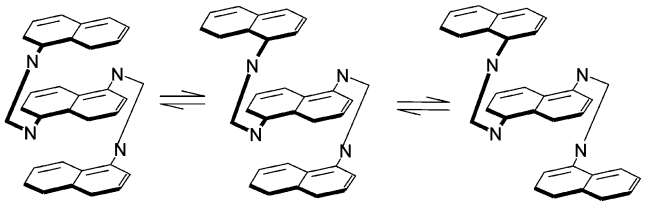


FIGURE 4. Schematic representation of the three conformers in the ^{Nap}**K(3)** obtained by rotation around the C−N bond between the naphthalene and urea units. Benzyl groups and end groups have been omitted for clarity. The conformers on the left and right are both present in the crystal structure of the compound. Dynamic ^{1}H NMR studies show that interconversion between the structures becomes rapid in solution above 400 K.

The cyclic hexamer ^{Phe}**K(6)** has a much simpler ^{1}H spectrum than the linear trimer and 9-mer. Singlets are observed for the protons on the central 1,4-diaminobenzene rings and for the benzyl groups, in accordance with the symmetry of the structure.

In the case of ^{Nap}**K(3)**, the protons from the naphthalene units give rise to rather broad resonances at 300 K while the benzyl group signals are partly resolved. Spectra obtained with 10-deg intervals from 300 to 420 K show that the naphthalene signals first broaden even more then become sharper until a well-defined pattern that can be assigned is established above 400 K. This behavior is typical of a dynamical system and we interpret this temperature dependence being due to rotations around the C−N bonds between the naphthalene and urea units. From the X-ray crystallographic structure of this compound, which will be discussed later, it is evident that two types of face-to-face geometries between the naphthalene units are possible. They are either fully or partially eclipsed, leading to three different conformers for this system as shown in Figure 4.

The ^{1}H spectrum of 1,5-bischlorocarbamoyl-*N*,*N*′-dibenzylaminonaphthalene (**5**) shows two doublets at 4.23 and 5.44 ppm that can be assigned to each of the protons in the benzyl-methylene groups. This splitting is due to the locked conformation around the C−N bond also seen in the X-ray structure (see Figure 5). This is in contrast to the spectrum of the 1,5-dibenzylaminonaphthalene (**2**) where only one resonance at 4.54 ppm is observed. It can therefore be concluded that the introduction of the carbamoyl group restricts the geometry around the C−N bond so that only torsion angles around 90° are allowed. In the ^{13}C spectrum of compound **5** some of the resonances are split in two. This indicates that two atropisomers are present with the groups on the two nitrogen atoms arranged in either cis or trans configuration. Similar atropisomerism was observed by Julia et al. for a series of *N*-aryl-*N*-benzyl alkyl carbamates.[7] When the aryl group was a substituted phenyl group the NMR coalescence temperature was in the range 300−400 K, and with naphthyl derivatives it was above 400 K. This is in accordance with the values obtained in this study.

The Solid State. As documented by the NMR studies in solution the geometry of the simple chlorocarbamoyl monomers is a locked conformation that exhibits hindered rotation. The solution of the crystal structures for **5** and **6** confirmed this expectation. Extensive studies of the effect on the molecular geometry upon alkylation of *N*-arylarylamides and *N*,*N*′-dialkyl-*N*,*N*′-diarylureas have shown the geometry to be very different from that of the corresponding NH-amides and NH-ureas. There is only one example of an *N*-benzyl-*N*-arylarylamide[8] in the CSD[9] (Cambridge Structure Database) that can serve for comparison with the structures presented here (there is one additional cyclic structure with a locked geometry[10] and one additional structure not found in the database).[11] There are no examples of *N*,*N*′-dibenzyldiarylureas. Most studies of *N*-alkylation on these systems have been based on *N*-methylation.[12] In **5** the chlorine atoms of the two substituents are on opposite sides of the plane of the naphthalene ring as shown in Figure 5. This is in direct opposition to the geometry observed when the aromatic system is a 9,10-disubstituted anthracene molecule. It is interesting to note that two positions of the benzyl groups, which correspond to energy minima, exist and

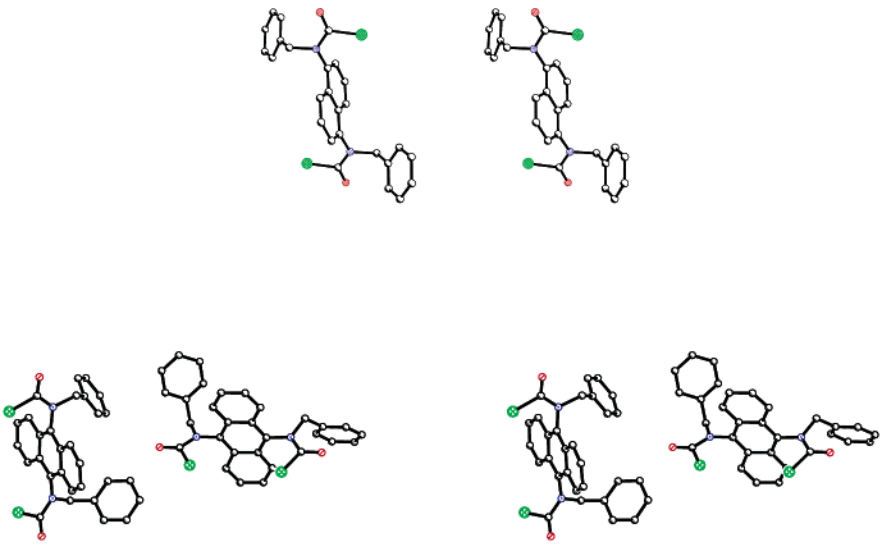


FIGURE 5. Stereoviews of the **5** (above) and **6** (below) systems. While the two benzyl substituents are on opposite sides of the plane of the naphthalene system in **5** they are on the same side of the plane of the anthracene system in **6** when both of the molecular geometries are observed in the asymmetric unit.

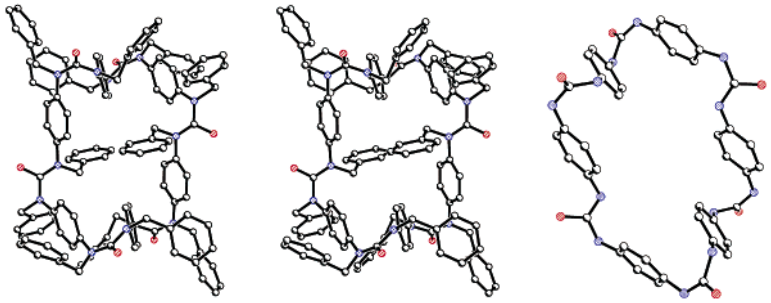


FIGURE 6. On the left is a stereoview showing the geometry of the ^{Phe}**K(6)** cyclic hexamer. On the right benzyl groups have been omitted to clearly show the backbone.

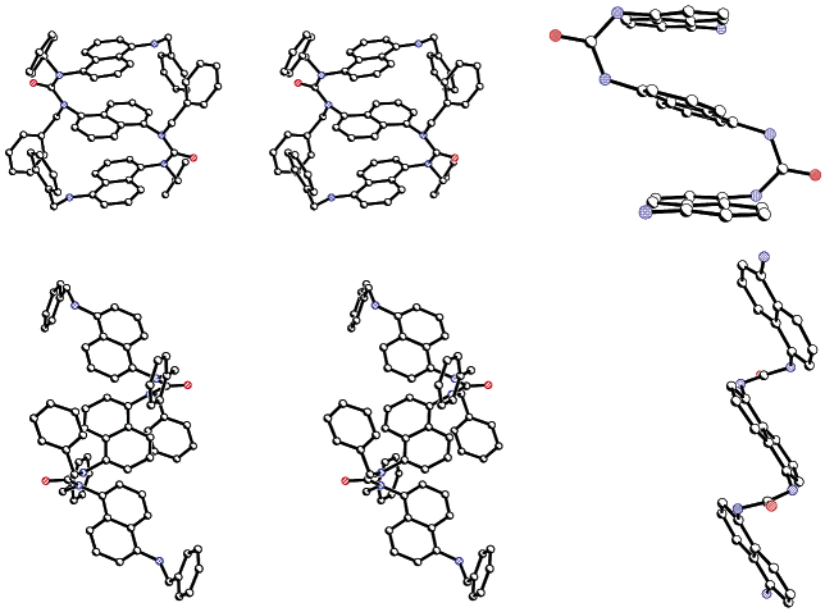


FIGURE 7. On the left are stereoviews showing the geometry of the two possible conformers observed in the asymmetric unit of ^{Nap}**K(3)**. On the right monoviews show the cisoid (top) and transoid (bottom) configurations of the backbone with benzyl groups and hydrogens omitted for clarity.

both are observed in the solid state. This is also the reason that there are two molecules in the asymmetric unit, and while this is normally considered rare or indicative of overseen symmetry in the structure solution procedure, this is an example of two geometrically distinct molecular entities in the asymmetric unit that are not related by symmetry. It is also noteworthy that the benzyl groups and the chlorine atoms prefer to be situated at the same side of the plane of the anthracene ring in the crystal.

The advantage of the ^{Phe}**K**-oligomers is that there is no obvious possibility of having conformers. This is supported by the NMR studies of both the ^{Phe}**K(3)** and ^{Phe}**K(9)** system where all the signals are well resolved. The system must however be considered to be moderately flexible at least during the conditions of the synthesis (boiling collidine at 180 °C). This is supported by the formation of some cyclic oligomers for the ^{Phe}**K** system. These oligomers were observed on the SEC (Solvent Exclusion Chromatography) trace and while it was clear from the molecular mass obtained this way during the synthesis of ^{Phe}**K(9)** from ^{Phe}**K(3)** and **4** that it would have to be the ^{Phe}**K(6)** it was not until a tiny amount of this byproduct was isolated by preparative SEC and

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TABLE 1. Crystallographic Data for Compounds 5, 6, ^{Nap}K(3), and ^{Phe}K(6)$_{cyclic}$

compd	**5**	**6**	^{Nap}**K(3)**	^{Phe}**K(6)$_{cyclic}$**
formula	$C_{33}H_{28}N_2O_2Cl_2$	$C_{30}H_{22}N_2O_2Cl_2$	$C_{74}H_{62}N_6O_2$	$C_{150}H_{164}N_{12}O_6$
formula wt	555.47	513.40	1067.30	2230.93
crystal system	triclinic	triclinic	triclinic	tetragonal
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$I4_1/\mathbf{a}$
Z	1	4	2	8
a, Å	8.7748(9)	12.186(2)	11.7054(14)	37.842(14)
b, Å	9.2451(9)	13.548(3)	15.5692(19)	37.842(14)
c, Å	9.9577(10)	16.948(3)	15.9976(19)	16.208(13)
α, deg	70.518(2)	69.354(14)	74.834(3)	90
β, deg	84.189(2)	74.221(14)	85.802(2)	90
γ, deg	65.367(2)	89.874(16)	81.981(2)	90
V, Å^3	691.58(12)	2505.9(8)	2784.4(6)	23209(22)
ρ, g cm^3	1.334	1.361	1.273	1.277
cryst dimens, mm^3	0.50 × 0.25 × 0.13	0.75 × 0.50 × 0.25	0.50 × 0.27 × 0.15	0.75 × 0.37 × 0.37
type of radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ, cm^{-1}	0.269	0.290	0.077	0.078
T, K	120(2)	120(2)	120(2)	120(2)
no. of reflns	9007	32293	36320	150010
no. of unique reflns	3709	13301	14899	16722
$R(F)$, $R_w(F^2)$ all data	0.0383, 0.0925	0.0827, 0.2595	0.0593, 0.1419	0.2405, 0.6444

crystallized that MALDI-TOF showed it to have a mass that was ^{Phe}**K(6)** + 26 (+CO − 2H). This was fully appreciated to be the cyclic hexamer through crystallization and crystal structure solution. While the physical quality of the crystals was very poor, which gave poor crystallographic data, it was possible to solve the structure and show that the overall geometry of the molecule is cyclic. Figure 6 is a stereoview of the cyclic hexamer obtained from the crystal structure. It is interesting to compare the geometry of the cyclic ^{Phe}**K(6)** molecule with that of many of the well-studied macrocycles such as the cyclophanes (calixarenes, recorsinarenes, etc.) and the cyclodextrins.

While the ^{Phe}**K** system was considered flexible the ^{Nap}**K** system was considered to be less flexible because of the steric demand and rigidity of the naphthalene unit. The fact that the naphthalene is 1,5-disubstututed also hosts the possibility of different conformers as shown in Figure 4. Crystal structure solution of single crystals of ^{Nap}**K(3)** showed both possible conformers in the asymmetric unit. The reason for this is ascribed to serendipity and it is difficult to say whether one conformer will predominate when the oligomers become larger. Figure 7 shows the geometry of the two conformers in the asymmetric unit.

Again while there are two molecules in the asymmetric unit this is understandable as they are crystallographically distinct molecules that are not related by symmetry.

Conclusion

Two series of oligomers based on 1,4-dibenzylaminobenzene and 1,5-dibenzylaminonaphthalene have been prepared and characterized both in solution and in the solid state. *N*-Alkylation with benzyl groups has been demonstrated to have the same type of structure generating effect as methyl groups. This effect changes the transoid geometry of substituted ureas with remaining hydrogens on both nitrogen atoms into a structure with the aryl groups overlapping in a face-to-face arrangement. Interesting dynamic behavior was observed especially in the case of the 1,5-diaminonaphthalene derivatives, leading to two different types of stack-like orientations. When several of these substituted urea fragments are coupled together zigzag stacks are obtained. Although some structural flexibility is allowed, they have a well-defined predictable structure with amine groups at both ends suitable for further elaboration. Such entities are reminiscent of domains in protein structures and we could envisage a similar role for large building blocks such as those created in this work.

Experimental Section

***N,N′*-Dibenzylbenzene-1,4-diamine (1).**[4] 1,4-Diaminobenzene (108 g, 1 mol) and benzaldehyde (210 g) were mixed in absolute ethanol (250 mL). The mixture became warm and a thick mass formed. It was then suspended in THF (1 L) and glacial acetic acid was added (500 mL). The imine was then reduced by careful addition of sodium borohydride (70 g) until the yellow/green coloration of the imine disappeared. Water was then added carefully and the phases were separated. The dark organic phases were concentrated in a vacuum. The dark product was recrystallized from toluene/heptane (5 L). Yield 288 g (100%) as colorless plates. ^{1}H NMR ($CDCl_3$, 250.1 MHz, 300 K) δ 3.69 (br s, 2H), 4.32 (s, 4H), 6.64 (s, 4H), 7.29−7.46 (m, 10H). Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 82.77; H, 6.92; N, 9.66.

***N,N′*-Dibenzyl-1,4-bis(chlorocarbonylamino)benzene (4).** Compound **1** (2.9 g, 10 mmol) was added to a phosgene solution (20 mL, 20% in toluene) and triethylamine (5 mL). The mixture was heated under reflux for 30 min and then evaporated to dryness. The salts were removed by trituration with water and the tan compound recrystallized twice from CCl_4. Yield (3.1 g, 75%); mp 126−7 °C; ^{1}H NMR ($CDCl_3$, 250.1 MHz, 330 K) δ 4.91 (s, 4H), 7.02 (s, 4H), 7.1−7.2 (m, 4H), 7.28−7.33 (m, 6H). Anal. Calcd for $C_{22}H_{18}Cl_2N_2O_2$: C, 63.93; H, 4.39; N, 6.78. Found: C, 63.98; H, 4.13; N, 6.63.

^{Phe}K(3). Compound **1** (25 g, 86.7 mmol) and Cs_2CO_3 (60 g, 0.184 mol) were mixed with phosgene (125 mL, 20% in toluene). A slight pink coloration was observed. Dichloromethane (200 mL) was added and the mixture was stirred for 0.5 h. The mixture was evaporated to dryness and compound **1** (50 g, 0.173 mol) was added along with distilled collidine (250 mL). The reaction was followed with SEC and stopped after 3 h where complete conversion was observed. The collidine was evaporated and the residue slurried with water and filtered and washed with light petroleum. The material was recrystallized from toluene (1.6 L). Yield 38.65 g (49%); mp >260 °C; ^{1}H NMR ($CDCl_3$, 250.1 MHz, 300 K) δ 3.61 (t, 2H, J = 4 Hz), 4.04 (d, 4H, J = 4 Hz), 4.51 (s, 4H), 4.53 (s, 4H), 5.88 (d, 4H, J = 9 Hz), 6.09 (d, 4H, J = 9 Hz), 6.15 (s, 4H), 7.1−7.25 (m, 30 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz,

300 K) δ 48.6, 55.7, 56.1, 112.8, 127.1, 127.4, 127.8, 128.5, 128.6, 128.7, 129.0, 129.3, 134.5, 139.0, 139.4, 139.5, 142.1, 146.0, 161.8. Anal. Calcd for $C_{62}H_{56}N_6O_2$: C, 81.19; H, 6.15; N, 9.16. Found: C, 80.99; H, 6.03; N, 8.97.

^{Phe}K(9) and the Cyclic ^{Phe}K(6). ^{Phe}K(3) (5 g, 5.5 mmol) was placed in a dried flask containing Cs_2CO_3 (16 g, 49 mmol) and methylene dichloride (50 mL). Phosgene (20 mL, 20% in toluene) was added and the mixture was stirred at 25 °C for 30 min. The mixture was then evaporated to dryness. **^{Phe}K(3)** (10 g, 11 mmol) was mixed with collidine (100 mL distilled from CaH_2, must be very dry). The mixture was heated and a few milliliters of collidine to remove the last traces of moisture. This solution was then added to the acid chloride and heated to reflux. The reaction was stopped after 4.5 h where **^{Phe}K(9)** was the major product. The mixture was cooled and poured into water (600 mL) and washed out of the flask with toluene (100 mL). After being stirred for 10 min the mixture was filtered and the white powder washed with ether and light petroleum. The raw product was then purified in the following way: The solid was stirred in boiling toluene (600 mL) and left at ambient temperature until the next day where the product was filtered and washed with toluene and then petroleum ether. A tiny amount of crystals later formed in the washings. These were isolated by filtration and dried (0.2 g). X-ray crystallography and mass spectrometry (MALDI-TOF) showed this product to be the pure cyclic **^{Phe}K(6)**. Anal. Calcd for $C_{126}H_{108}N_{12}O_6 \cdot (H_2O)_2$: C, 78.73; H, 5.87; N, 8.74. Found: C, 78.92; H, 5.84; N, 8.92. ^{1}H NMR ($CDCl_3$, 250.1 MHz, 300 K) δ 4.46 (s, 24H), 6.46 (s, 24H), 7.0−7.1 (m, 24H), 7.15−7.22 (m, 36H); ^{13}C NMR ($CDCl_3$, 62.9 MHz, 300 K) 55.6, 121.6, 126.8, 127.7, 138.2, 141.8, 161.1.

The solid product (6.42 g) filtered from the trituration with toluene was then crystallized from mesitylene to give the pure **^{Phe}K(9)**. Yield 0.51 g; mp >260 °C. The mother liquor still contained most of the product. Anal. Calcd for $C_{188}H_{164}N_{18}O_8$: C, 80.54; H, 5.90; N, 8.99. Found: C, 80.25; H, 5.68; N, 8.93. ^{1}H NMR ($CDCl_3$, 250.1 MHz, 300 K) δ 3.77 (s, 2H), 4.06 (s, 4H), 4.63 (br s, 24H), 4.74 (s, 4H), 4.82 (s, 4H), 5.99 (br s, 24H), 6.16 (d, 4H, J = 8 Hz), 6.28 (d, 4H, J = 8 Hz), 6.35 (d, 4H, J = 8 Hz), 7.2−7.3 (m, 90H).

***N,N′*-Dibenzylnaphthalene-1,5-diamine (2).**[4] Naphthalene-1,5-diamine (100 g, 0.632 mol) and benzaldehyde (74 g, 10% excess) were mixed neat with a little acetic acid to prepare the imide. THF (1 L) was added together with acetic acid (180 mL). The mixture was cooled on an ice-bath and stirred vigorously while $NaBH_4$ (56 g, 1.48 mol) was added in small portions. (**Caution!** The reaction is exothermic and hydrogen is evolved.) After 1 h water was added (2 L) slowly to avoid excessive foaming. Separation of the raw product by filtration followed by recrystalization from toluene (5 L) gave the product **3** as a white powder. Yield 375 g (80%); mp 187−8 °C; ^{1}H NMR ($CDCl_3$, 250.1 MHz, 300 K) δ 4.54 (s, 4H), 4.78 (s, 2H), 6.68 (d, 2H, J = 7 Hz), 7.27−7.52 (m, 14H). Anal. Calcd. for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28. Found: C, 84.89; H, 6.46; N, 8.29.

***N,N′*-Dibenzyl-1,5-bis(chlorocarbonylamino)naphthalene (5).** 1,5-Dibenzylaminonaphthalene (**2**) (34 g, 0.10 mol) was placed in a flask containing chloroform/toluene (1:1) (200 mL) and triethylamine (40 mL, 0.54 mol). Phosgene (150 mL, 20% in toluene) was added. The mixture became warm and the color changed to a deeper yellow. A precipitate of the triethylammonium hydrochloride formed. After 1h the mixture was washed with water and dried ($MgSO_4$). The phase was evaporated to dryness and the product recrystallized from toluene (400 mL). It was left in the freezer overnight. After the product was filtered and washed with light petroleum it was dried in the vacuum oven at 80 °C for 4 h. Yield 46 g (99%); mp 178−9 °C; ^{1}H NMR ($CDCl_3$, 250.1 MHz, 300 K) δ 4.53 (d, 2H, J = 14 Hz), 5.44 (d, 2H, J = 14 Hz), 7.10 (d, 2H, J = 8 Hz), 7.2−7.33 (m, 10H), 7.46 (t, 2H, J = 8 Hz), 7.81 (d, 2H, J = 8 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz, 300 K) δ 56.7, 124.0, 127.3, (128.4, 128.5), 128.8, (129.0, 129.1), 129.9, 131.7, (135.7, 135.8), (150.8, 150.9), numbers in parentheses are due to atropisomerism. Anal. Calcd for $C_{26}H_{20}Cl_2N_2O_2$: C, 67.40; H, 4.35; N, 6.05. Found: C, 67.37; H, 4.26; N, 6.09.

^{Nap}K(3). Cesium carbonate (50 g, 155 mmol) was dried in an oven at 150 °C for 4 h to remove water. In a dried flask cesium carbonate and collidine (500 mL, freshly distilled) were mixed together with compound **2** (75 g, 220 mmol) and compound **5** (50 g, 110 mmol). The reaction mixture was heated to reflux under argon for 18 h and then left to cool overnight. Water (0.5 L) was added with stirring and the slurry was filtered. The product was triturated with more water, filtered, and washed with petroleum ether. Finally the product was recrystallized from toluene (2 L). Yield 57.5 g (49%); mp >260 °C; ^{1}H NMR ($CDCl_3$, 250.1 MHz, 300 K) δ 4.45 (s, 2H), 4.58 (s, 4H), 5.10 (s, 4H), 5.17 (s, 4H), 6.24 (d, 2H, J = 8 Hz), 6.51 (d, 2H, J = 7 Hz), 6.68 (t, 4H, J = 8 Hz), 6.80 (t, 2H, J = 4 Hz), 7.18−7.55 (m, 32H), 7.64 (d, 6H, J = 7 Hz). Anal. Calcd for $C_{74}H_{62}N_6O_2$: C, 83.27; H, 5.86; N, 7.87. Found: C, 83.25; H, 5.83; N, 7.87.

^{Nap}K(9). ^{Nap}K(3) (6 g, 5.6 mmol) was placed in a dried flask containing Cs_2CO_3 (10 g, 31 mmol) and commercial collidine (100 mL). Phosgene (6.0 mL, 20% in toluene) was added and the mixture was stirred at 100 °C for 15 min when **^{Nap}K(3)** (12 g, 11.2 mmol) was added and the first sample for SEC drawn. The mixture was then heated to reflux. After 24 h the reaction has stopped and the major component was starting material **^{Nap}K(3)**. The mixture was left to cool. Acetone (100 mL) was added, the mixture was stirred and then poured into water (1 L), and the crystalline compound was filtered and washed with water (2 × 250 mL), ether (3 × 200 mL), and light petroleum (100 mL). The product was then boiled in toluene (1 L) for 30 min and filtered. Yield 14 g, 77%. An analytical sample was obtained by repeated fractional crystallization from mesitylene. Mp >260 °C. Anal. Calcd for $C_{224}H_{182}N_{18}O_8 \cdot (H_2O)_3$: C, 81.33; H, 5.73; N, 7.62. Found: C, 81.32; H, 5.61; N, 7.31.

9,10-Dibenzylaminoanthracene (3). 9,10-Bis(*N*-benzylformamido)anthracene was prepared from 9,10-diformylaminoanthracene[6] by alkylation with benzyl chloride and an excess of *t*BuOK in THF. A satisfactory elemental analysis could not be obtained for this compound, but it was pure enough to use directly in the next step. 9,10-Bis(*N*-benzylformamido)anthracene (30 g, 67.5 mmol), KOH (85%, 60 g), and ethanol (120 mL) were refluxed under argon; the mixture becomes dark red and after 20 min a thick homogeneous solution had formed. It was difficult to isolate the product and many attempts were made. It was found that (probably) 9,10-bisbenzalimine was formed (2.6 g obtained upon recrystalization from toluene as bright red needles). When the toluene liquor was reduced with a little $NaBH_4$ the color turned dark green (probably due to the reduction of the alleged acceptor imine). When this was filtered through silica a bright yellow compound was obtained. Yield 7 g, 27%; mp 120−2 °C; ^{1}H NMR ($CDCl_3$, 250.1 MHz, 300 K) δ 3.8 (br s, 2H), 4.49 (s, 4H), 7.4−7.52 (m, 10H), 7.61 (d, 4H, J = 7 Hz), 8.3−8.37 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz, 300 K) δ 56.6, 124.0, 125.4, 126.3, 127.0, 127.6, 127.8, 128.4, 129.1, 134.5, 137.4, 140.7.

***N,N′*-Dibenzyl-9,10-bis(chlorocarbonylamino)anthracene (6).** The amine **3** (1 g, 2.6 mmol) was mixed with phosgene (10 mL, 20% in toluene) and triethylamine (5 mL) in methylene chloride (100 mL). The mixture was stirred for 1 h. A precipitate had formed. The mixture was poured into water (100 mL) and the organic phase was separated, dried ($MgSO_4$), and evaporated to give a dark oil (toluene and triethylamine); light petroleum (50 mL) was added giving a precipitate that was filtered (0.5 g), which contained the product and some impurities. When light petroleum wss added to the liquor yellow crystals formed slowly, whcih was found to be the pure product. Yield 0.4 g (30%); mp 139−40 °C; ^{1}H NMR ($CDCl_3$, 250.1 MHz, 300 K) δ 5.09 (s, 4H), 6.94 (d, 4H, J = 7 Hz), 7.10 (t, 4H, J = 7 Hz), 7.21 (d, 2H, J = 7 Hz), 7.38−7.42 (m, 4H), 7.65−7.71 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz,

300 K) δ 57.3, 123.7, 127.7, 128.7, 128.8, 129.5, 130.8, 134.3, 134.9, 151.5. Anal. Calcd for $C_{30}H_{22}Cl_2N_2O_2 \cdot H_2O$: C, 68.97; H, 4.44; N, 5.36. Found: C, 68.97; H, 4.42; N, 5.65.

Crystallography. General crystallographic data can be found in Table 1. The crystals were drawn directly from the mother liquor, coated with a thin layer of protecting oil, and mounted on glass fibers with use of Apiezon grease and transferred quickly to the cold stream of nitrogen (Oxford Cryostream) on the diffractometer (Siemens SMART CCD Platform). Crystals of **5** and cyclic ^{Phe}**K(6)** lost solvent upon exposure to air and this impaired the quality of the data due to a degradation of the crystalline properties. In compound **5** the solvent toluene molecule was situated close to the center of symmetry, which was modeled as two toluene solvent molecules with a sof of 0.5. The cyclic ^{Phe}**K(6)** crystallizes in the tetragonal spacegroup $I4_1/a$. This gives rise to large channels extending throughout the crystal along the unique axis that contains solvent hexane molecules. Similar problems with poor data quality due to crystal degradation have been observed in similar crystallographic problems with solvent-containing channels in calixarenes.[13] Further the problems associated with larger observed *R*-factors for crystals with many weakly scattering atoms in the asymmetric unit have been shown.[14] The solution to this structure was particularly problematic, and while the quality of the data does not allow any detailed crystallographic detail to be extracted, the connectivity, molecular conformation, and packing properties could be determined. The benzene rings were constrained to approach a hexagon and the symmetry constraints on the solvent hexane molecules positioned close to a center of symmetry were modeled by neglecting the symmetry constraints and keeping the sof at a value of 1. In the case of **6** and ^{Nap}**K(3)** two molecules were found in the asymmetric unit, and while this is normally considered rare the molecular conformation of the two different molecules was distinct, making the consideration of overseen symmetry unnecessary. An almost complete sphere of reciprocal space was covered by a combination of several sets of exposure frames: each set with a different φ angle for the crystal and each frame covering a scan of 0.3° in ω. Data collection, integration of frame data, and conversion to intensities corrected for Lorenz, polarization, and absorption effects were performed with the programs SMART,[15] SAINT,[15] and SADABS.[16] Structure solution, refinement of the structures, structure analysis, and production of crystallographic illustrations were carried out with the programs SHELXS97,[17] SHELXL97,[17] and SHELXTL.[18] The structures were checked for higher symmetry and none was found.[19] In all of the structures H atoms were included and their calculated positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-186137, CCDC-186138, CCDC-186139, and CCDC-186140. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

Acknowledgment. This work was supported by the Danish Technical Science Foundation of Denmark (STVF).

Supporting Information Available: Tables of fractional coordinates, equivalent isotropic and anisotropic thermal parameters, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

JO025980F

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