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New [4.4]Cyclophanes: Molecular Parallelograms, Triangles, Rhombuses, Pentagons, and Supramolecular Constructions

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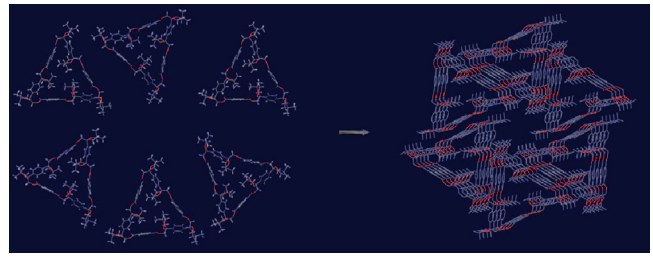

The fair or good yield synthesis of new [(4.4)^n]cyclophanes (n = 1−5), starting from 1,4-bis(2-hydroxymethyl-5,5-dimethyl-1,3-dioxan-2-yl)benzene and several diacid−dichlorides, based on monomer and oligomer formation reactions (from 1 + 1 to 5 + 5), is reported. The structure and the complex architectures of the lattices for these cyclophanes are revealed by the X-ray molecular structure for five compounds, NMR investigations, and mass spectrometry measurements. Intramolecular and intermolecular CH−π, p−π, and π−π interactions are observed, both in solid state and solution.

Introduction

[4.4]Cyclophanes[1] exhibit properties which are on average between those of classic [2.2]cyclophanes (in which the aromatic units are close one to the other and display strong π−π interactions)[2] and the large cyclophanes (in which the aromatic units are connected by larger bridges and the interactions between the aromatic units are considerably weaker).[3] The rotation of the aromatic units is completely hindered in [2.2]cyclophanes, and it is more or less free for large cyclophane derivatives.[2,3]

The length of the bridges in [4.4]cyclophanes allows, both in monomers and oligomers, the π−π and/or CH−π interactions between the aromatic units as well as the interactions between different groups (e.g. ester) belonging to the bridges and the aromatic components of the cyclophanes.[4]

The macrocyclization reactions between two compounds (nS + nR; S = substrate, R = reagent) can lead to monomers (n = 1) and/or oligomers (n > 1).The ratio between monomers and oligomers depends upon the *preorganization* of the substrate,

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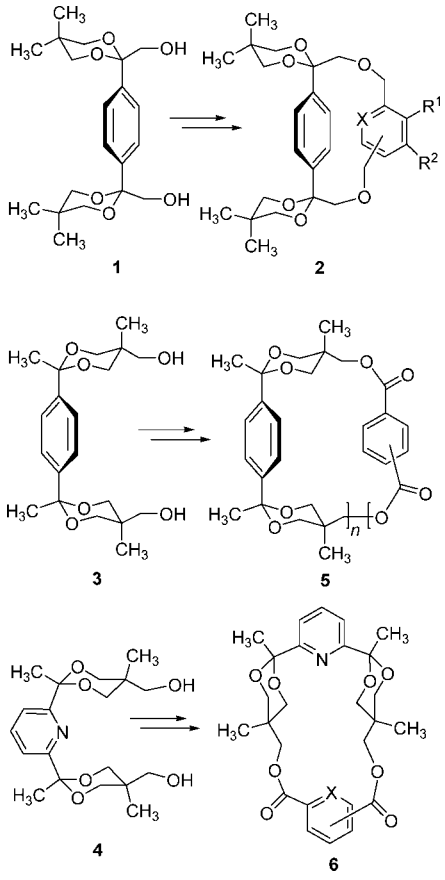
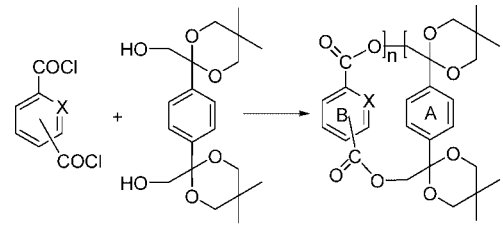
SCHEME 1



SCHEME 2



1 X=CH, *meta* 7
X=CH, *para* 8
X=N, *2,6-pyridilene* 9

n=1 (**a**), n=2 (**b**),n=3 (**c**), n=4 (**d**),n=5 (**e**)

TABLE 1. Results for the Synthesis of Cyclophanes 7−9

	position of the bridges	X	*n*	macrocycle	yields* (%)
7a	meta	CH	1	monomer	50
7b	meta	CH	2	dimer	18
7c	meta	CH	3	trimer	2
8b	para	CH	2	dimer	19
8c	para	CH	3	trimer	14
8d	para	CH	4	tetramer	12
8e	para	CH	5	pentamer	9
9a	2,6-pyridylene	N	1	monomer	46

* The yields are calculated for separated compounds. No others terms were observed in the MALDI-TOF spectra of the row products.

the steric complementarities between the substrate and the reagent, the mechanism of the macrocyclization reaction, and/or the efficiency of the *template*.[5]

We recently reported some new [4.4]cyclophanes **2** (Scheme 1)[6] obtained by the etherification of 1,4-bis(2-hydroxymethyl-5,5-dimethyl-1,3-dioxan-2-yl)benzene **1** with several bis(bromomethyl)arenes and some new [7.7]cyclophanes[7] **5** and **6** obtained by the esterification reactions of bis(2,5-dimethyl-5-hydroxymethyl-1,3-dioxan-2-yl)arenes (**3** and **4**) with aromatic diacid dichlorides. Diols **1**, **3**, and **4** exhibit an axial−axial orientation of the aromatic unit for both hetetocycles which ensure the *preorganization* of the substrate (favorable structure) for the macrocyclization reaction. The etherification macrocyclization reactions proceed in fair or good yields (34−67%) to produce monomeric [4.4]cyclophanes (1 + 1 reaction). The synthesis of **5** and **6** by esterification macrocyclization reactions proceeded with good yields (27−52%), producing monomers, dimers, and trimers in different ratios; the oligomerization state is correlated with the structure of the reagent [ortho, meta (or 2,6-pyridylene), and para positions of the acid chloride groups] and of the substrate [the positions of the 1,3-dioxane units at the aromatic ring (*p*-phenylene or 2,6-pyridylene)].

We describe herein the synthesis of new [4.4]cyclophanes. The key synthetic step was the reaction between diol **1** and aromatic diacid dichlorides. In order to investigate the influence of the more rigid bridges (exhibiting an sp^2 carbon atom in a planar ester COO− group) on the monomer/oligomers ratio, on the conformational equilibria of these ester [4.4]cyclophanes, and on the intramolecular and intermolecular CH−π, $\pi-\pi$, and p−π interactions.[8]

Results and Discussion

New macrocyclic ester [(4.4)^n]cyclophanes **7**−**9**, monomers (n = 1), and oligomers (from dimers to pentamers; n = 2−5) were obtained in good yields (Scheme 2, Table 1) starting from 1,3-dioxane diol **1**[6] and several diacid dichlorides. The syntheses were conducted under high dilution conditions and in the presence of DMAP as base and *template* (targeted for monomers).

For the compound series **7** and **9**, the monomers (**7a** and **9a**) were the major products, while for series **8** the monomer was not observed. For compound **8**, the yields of larger oligomers

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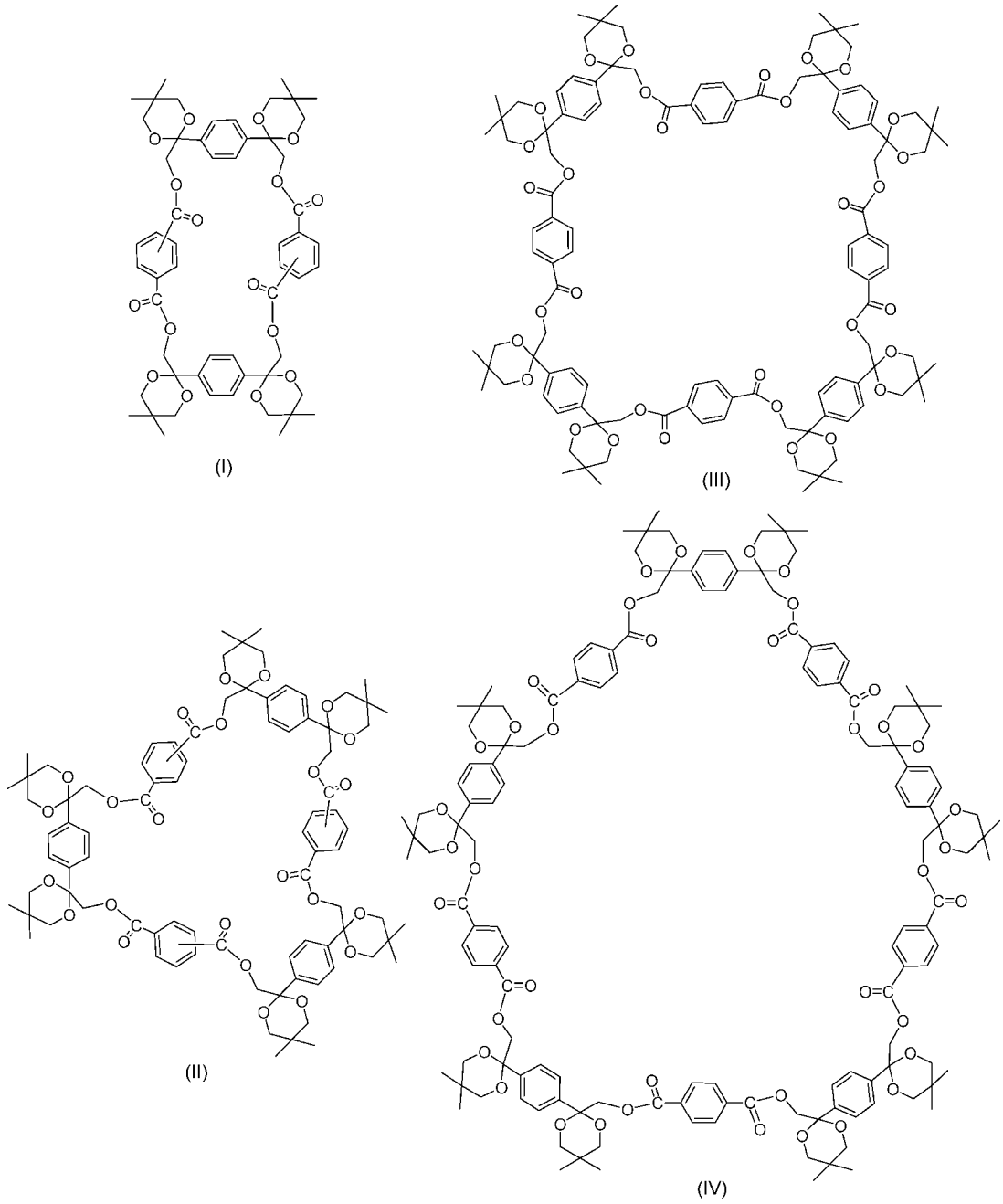
CHART 1. Structures of Dimers 7b (Meta) and 8b (Para) (I), Trimers 7c (Meta) and 8c (Para) (II), Tetramer 8d (III), and Pentamer 8e (IV)



(trimer, tetramer, and pentamer) are remarkably high, making this macrocyclization reaction particularly attractive for the synthesis of large host molecules. The obtained oligomers belong to the family of "rotanes".[9]

The dimers are [4]rotanes and the trimers are [6]rotanes, while the tetramer and the pentamer of **8** are [8]- and [10]rotanes, respectively (Chart 1). If [4]- and [6]rotanes are trivial,[10] [8]- and [10]rotanes can be considered to belong to the family of "exploded" [*n*]rotanes,[11] sharing similarities with the largest reported rotanes in the literature ([10]- and [12]rotanes).[11]

(9) [*n*]Rotanes are polyspiranes in which all the spiro atoms (*n*) belong to the same central ring, and in the name [*n*]rotanes, *n* represents the number of spirane units.

The dimers describe parallelograms; the trimers are triangles, while the large tetramer and pentamer are a rhombus and pentagon, respectively.

Structural Aspects in Solution. The NMR spectra of cyclophanes **7**−**9** are similar and quite simple. They exhibit different signals for the axial and equatorial protons at positions 4 and 6 of the dioxacyclohexane units and for the axial and equatorial methyl groups at position 5 of the heterocycles and reveal the anancomeric (rigid) conformational behavior of the 1,3-dioxane moieties and the axial orientation of the 1,4-phenylene unit for all 1,3-dioxane rings. This orientation of the aromatic ring was established on the basis of NOESY spectra (see the Supporting Information, Figure 12).

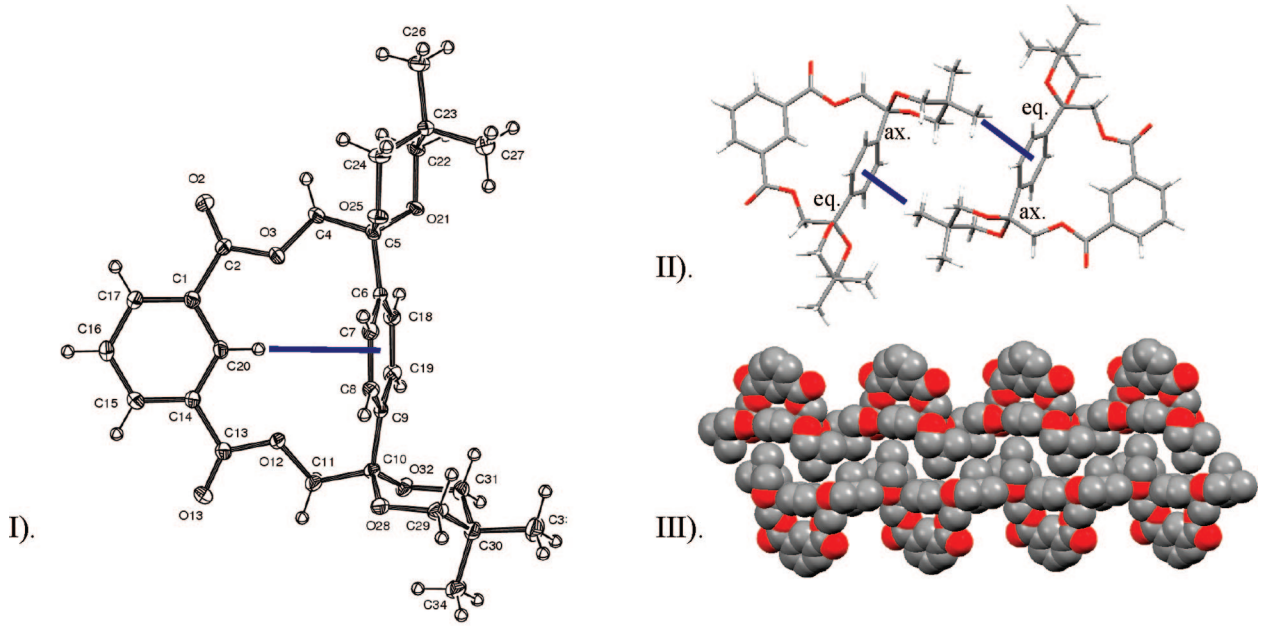


FIGURE 1. ORTEP diagram of compound **7a** (I) and Mercury representations (sticks and spacefill, respectively) of the dimer structures in the lattice (II) and of the zipper like arrangement of the cyclophanes in the view along the *a* crystallographic axis (III).

The spectrum at rt of **7a** (see the Supporting Information, Figure 10) exhibits only one AB system for the axial and equatorial protons of the heterocycles ($\delta_{ax} = 3.53$; $\delta_{eq} = 3.70$ ppm) and one singlet for the CH_2 groups ($\delta = 4.49$ ppm) of the bridges. The reduced number of signals in the NMR spectra at rt suggests the rapid rotation of the aromatic rings and the fast flipping of the bridges. In order to observe these conformational equilibria, in compound **7a**, variable-temperature NMR experiments were carried out (from 320 to 175 K) in $CDCl_3$ and THF-d_8 solutions. During all of these experiments, the spectra did not exhibit relevant modifications, and we concluded that the respective barriers for these equilibria are low and the corresponding conformational processes could not be frozen.

However, there are some other notable aspects of the NMR investigations. The comparison, in the ^{1}H NMR spectra (see the Supporting Information, Figure 11), of the positions of the signals belonging to the protons of the ortho-ortho′ positions of the 1,3-phenylene unit in the monomer (**7a**), dimer (**7b**), and trimer (**7c**) reveals the high shielding of the signal for monomer **7a** ($\delta_{7a} = 6.81$ ppm), the residual shielding for dimer **7b** ($\delta_{7b} = 8.24$ ppm), and the normal δ value for trimer **7c** ($\delta_{7c} = 8.57$ ppm). The shielding of this signal in the monomer and dimer is due to CH$-\pi$ interactions between the aromatic rings (disposed in *edge tilted to face* arrangements); these are stronger in the monomer, less important in the dimer, and insignificant in the trimer.

Similar differences could be observed between the chemical shifts of the signals pertaining to the protons of the aromatic ring of the ester part (B) of the oligomers **8b**, **8c**, **8d**, and **8e**. This signal is shielded for dimer **8b** ($\delta_{8b} = 7.59$ ppm), where the aromatic rings can be close one to the other, and they show similar and more deshielded δ values for the larger trimer ($\delta_{8c} = 7.99$ ppm), tetramer ($\delta_{8d} = 8.02$ ppm), and pentamer ($\delta_{8e} = 8.05$ ppm).

Structural Aspects in the Solid State: Molecular Parallelograms, Triangles, and Rhombuses. The single-crystal X-ray diffraction molecular structures were obtained for monomer **7a**, dimers **7b** and **8b**, trimer **8c**, and tetramer **8d**. The solid-state structural investigations revealed important intramolecular or intermolecular CH$-\pi$, $\pi-\pi$, or p$-\pi$ interactions that account for the peculiar shape of the molecules and the complex architectures of the lattices.

The ORTEP diagram for **7a** (Figure 1) shows the *edge-tilted to face* arrangement of the aromatic rings and reveals a low distance ($d = 3.0$ Å) between the ortho,ortho′ proton of the 1,3-phenylene unit (B) and the other aromatic ring of the cyclophane (A).

An important feature in the molecular structure of **7a** (Figure 1) is the conformational change of one of the dioxacyclohexane rings during the crystallization process. Thus, one of the dioxacyclohexane units is flipping during this process, and in the solid state, the *p*-phenylene ring adopts an axial (ax) orientation (as in solution or in the starting substrate) for one of the saturated heterocycles, while it adopts an equatorial (eq) orientation for the other one. Using the reported $\Delta G°$ values[12] for the conformational equilibria of 2-aryl,2-methyl-1,3-dioxanes (which show a large preference for the aromatic group in the axial orientation), one can be estimate at about $\Delta G° = 2.4$ kcal/mol enhancement of the system energy. This is due to the

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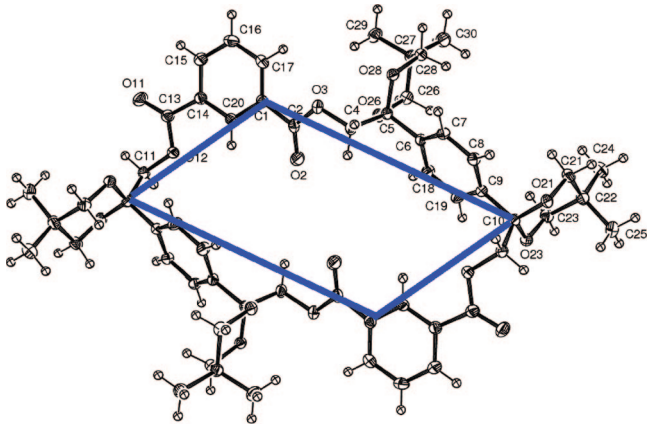

FIGURE 2. ORTEP diagram of **7b**.

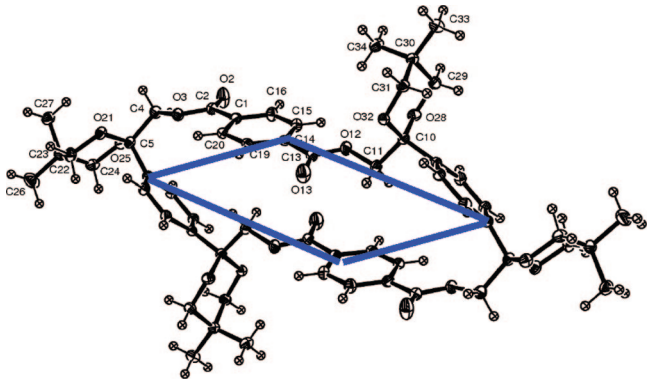

FIGURE 3. ORTEP diagram of **8b**.

conformational modification of one of the dioxacyclohexane units in **7a**, as described above. At the same time, flipping of one of the dioxacyclohexane rings makes possible the association of two molecules of axial−equatorial cyclophane into a dimer via CH−π interactions (the 1,4-phenylene units are less hindered in the equatorial−axial conformers than in the axial−axial ones; see the molecular structure of a similar diether cyclophane).[6] The CH−π interactions (Figure 1(II) and 1(III) involve the hydrogen atoms of the equatorial methyl group of the dioxacyclohexane ring with unmodified conformation of one cyclophane and the *p*-phenylene aromatic unit of the other cyclophane (the distances from the hydrogen atoms of the methyl group to the centroid of the *p*-phenylene ring are d = 3.26, 3.57, and 3.57 Å, respectively). The literature data estimate the stabilization of a molecular system by one CH−π interaction at $\Delta G^\circ = -0.6$ to -2.5 kcal/mol,[8b,13] so three CH−π interactions/mol can cover the energetical demand of the flipping of one of the dioxacyclohexane rings in cyclophane **7a**.

The molecular structures of dimers **7b** and **8b** (Figures 2 and 3) reveal the *parallelogram-like* shape of the formed macrocycles.

The analysis of these molecular structures reveals the parallel orientation of the similar aromatic rings and the influence of the $\pi-\pi$, p−π, and CH−π interactions on the structural behavior of the cyclophanes. For instance, in **8b**, the carbonyl groups are parallel and exhibit opposite orientations. The distance between the oxygen atom of a group and the carbon atom of the parallel group is d = 3.84 Å (see the Supporting Information and ref 8g), and the distances between the hydrogen

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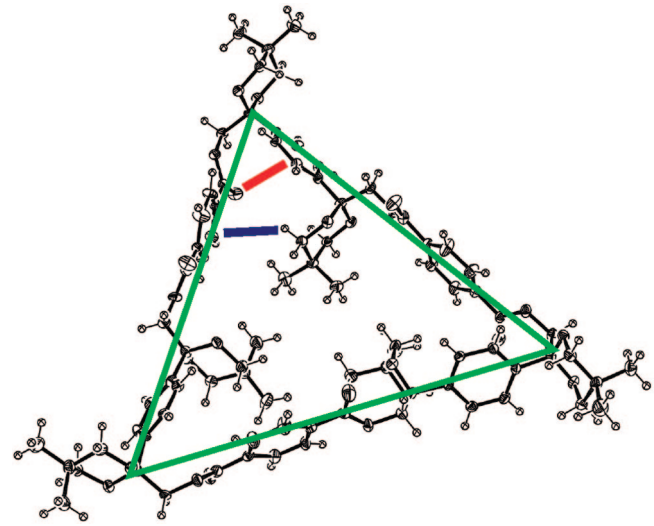

FIGURE 4. ORTEP diagram of the trimer **8c**.

atoms of the bridges (which are oriented inside the macrocycle) and the centroid of the opposite benzene ring are d = 3.265 and 3.367 Å, respectively. Other intramolecular and intermolecular interactions are shown in the Supporting Information.

The molecular structure of trimer **8c** (Figure 4) can be considered as a molecular triangle (for other molecular triangles see ref 14). Three of the 1,3-dioxane units are oriented inside the macrocycle, while the other three heterocyclic units exhibit an outside orientation.

This shape of **8c** molecules is the result of CH−π (shown in blue) and p−π (shown in red) interactions which involve one of the axial protons (at position 4 or 6) of the inside-oriented 1,3-dioxane units and the aromatic rings B (the distance to the centroid of B is 3.35 Å) and one of the carbonyl groups of the ester moiety and the aromatic ring A. The distance from the oxygen to the centroid of A is 3.52 Å and the angle between the plane of the aromatic ring A and the plane of C=O bond is 35.40, suggesting important interactions according to literature data.[8f]

The lattice (Figure 5) shows the formation of hydrophobic channels (visible in the projection along the a crystallographic axis) surrounded by six columns of molecules of trimer (I). This channel has a diameter of about 7.5 Å. This structure is built up by CH−π interactions between the molecules of neighboring columns (II). Such interactions are observed between the B aromatic rings (*offset face to face* arrangement) and between the hydrogen atoms of the axial methyl groups of the external 1,3-dioxane rings and the A aromatic units (II).

The molecular structure of tetramer **8d** (Figure 6) shows the formation of a molecular rhombus.[15] The similar aromatic rings

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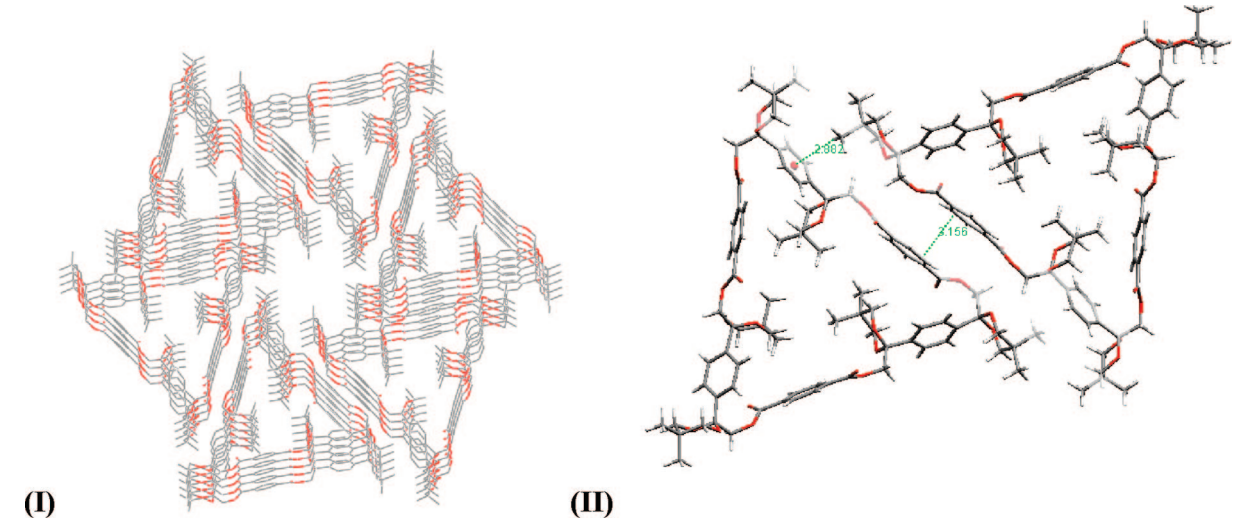

FIGURE 5. Mercury representation of the lattice of **8c** (view along the *a* axis, I), details of the intermolecular CH−π interactions (II).

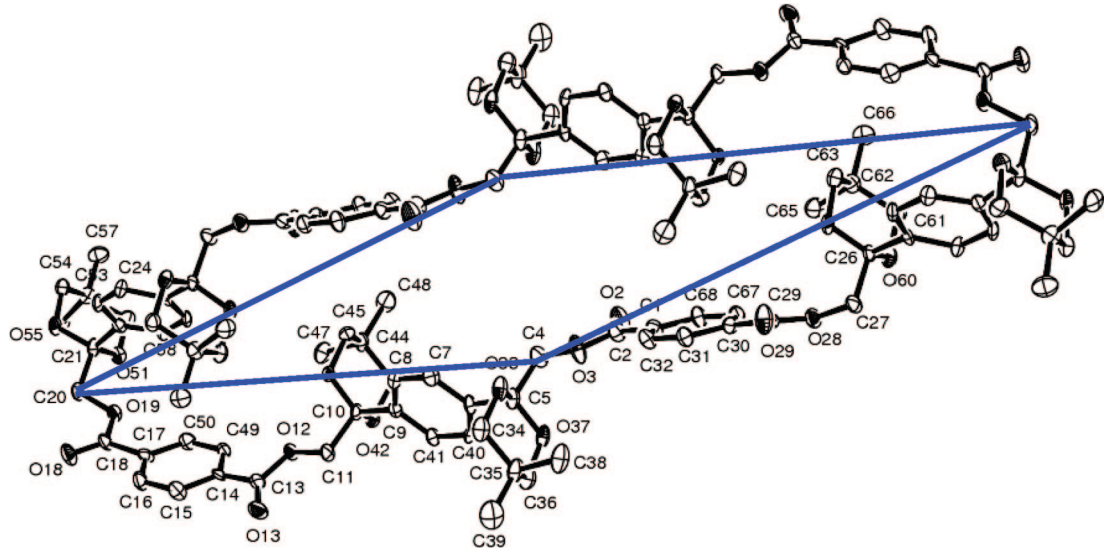

FIGURE 6. ORTEP diagram of tetramer **8d**.

are parallel two by two. Four dioxacyclohexane units are oriented inside the macrocycle and the other four 1,3-dioxane rings exhibit an opposite orientation (outside the macrocycle). The macrocycle exhibits a peculiar shape as the result of the important intramolecular CH−π interactions.

The distance from one hydrogen atom of one of the CH_2 groups of the dioxacyclohexane units (position 4 or 6) as well as that of one hydrogen atom of the equatorial methyl group of the same heterocycle to the center of ring B of the opposite side of the rhombus reveals CH−π interactions (CH_2, 3.16; CH_3, 3.29 Å). The investigations of the lattice show CH−π interactions and the inclusion of solvent molecules ($CHCl_3$) and the interactions with aromatic and carbonyl units[16] (see Figure 7 and the Supporting Information).

Conclusions

New [4.4]cyclophanes with ester groups in the bridges, from monomers to pentamers, were obtained in good or fair yields. The different compounds were separated by flash chromatography and were investigated as single compounds. The ratios between the different terms were correlated with the nature of the aromatic unit introduced by the diacid dichloride reagent: *m*-phenylene (mainly monomer, but also dimer and trimer), 2,6-pyridylene (only monomer), and *p*-phenylene (only oligomers, from dimer to pentamer).The oligomers exhibit peculiar shapes: the dimers are parallelograms and the trimers are triangles, while the tetramer and the pentamer of **8** are rhombus and pentagon, respectively. The structural investigations carried out by X-ray diffraction and NMR revealed important intramolecular and intermolecular CH−π and p−π interactions and the special organization of cyclophanes in the lattices with the formation of zippers and channels.

Experimental Section

General Procedure for the Synthesis of [4.4]Cyclophanes 2−4. A solution of *m*- or *p*-phthaloyl dichloride or pyridine-2,6-

U. *J. Org. Chem.* **2005**, *70*, 10147–10150. (b) Jeong, K. S.; Kim, S. Y.; Shin, U.-S.; Kogej, M.; Hai, N. T. M.; Broekmann, P.; Jeong, N.; Kirchner, B.; Reiher, M.; Schalley, C. A. *J. Am. Chem. Soc.* **2005**, *127*, 17672–17685. (c) Cotton, F. A.; Jin, J.-Y.; Li, Z.; L. Chun, Y.; Murillo, C. A. *Dalton Trans.* **2007**, *22*, 2328–2335.

(16) Swierczynski, D.; Luboradzki, R.; Dolgonos, G.; Lipkowski, J.; Schneider, H.-J. *Eur. J. Org. Chem.* **2005**, 1172–1177.

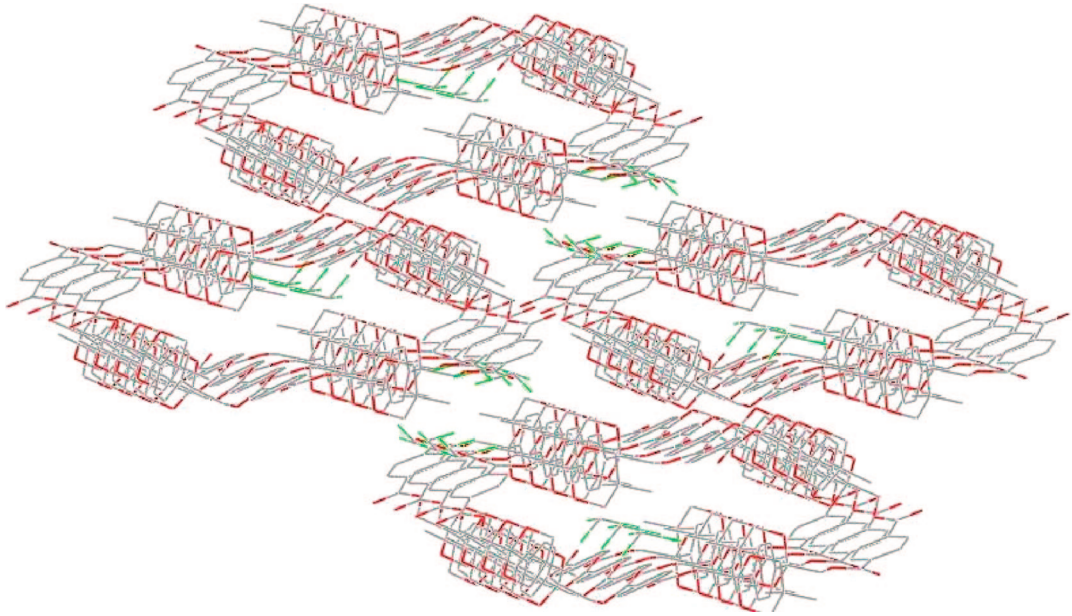

FIGURE 7. View of the lattice of compound **8d**.

dicarbonyl dichloride (0.66 mmol, 1.22 equiv) in dry THF (40 mL) was added with a high precision push-syringe over a period of 12 h to a well-stirred solution of diol **1** (0.54 mmol, 1.00 equiv) in dry CH_3CN (60 mL) and dry THF (15 mL) containing *N*,*N*′-dimethyl-4-aminopyridine (DMAP, 0.80 mmol, 1.48 equiv), the mixture was stirred at rt, and the reaction was monitored by TLC. Solvents were evaporated in vacuo, the residue was triturated with ether (100 mL), and the separated ether extract was evaporated in vacuo. The residue was purified by chromatography on silica gel to afford the target cyclophane.

Compound Characterization. 5,5;10,10-Bis[3′,3′-dimethyl-1′,5′-dioxapentane-1′,5′-diyl]-2,13-dioxo-3,12-dioxatricyclo[12.3.2^{6,9}.1^{1,14}]icosan-1(20),6,8,14,16,18-hexaene (7a): white crystals; yield 50% (134 mg, 0.27 mmol); mp 222−223 °C; purified by flash chromatography (silica gel, diethyl ether/pentane = 2:3); R_f = 0.88; ^{1}H NMR(300 MHz, $CDCl_3$) δ ppm: 0.72 (s, 6H, 3′-CH_{3eq}), 1.30 (s, 6H, 3′-CH_{3ax}), 3.53 (d, 4H, 2′-H_{ax}, 4′-H_{ax}, ^2J = 11.3 Hz), 3.70 (d, 4H, 2′-H_{eq}, 4′-$H_{eq,}$ ^2J = 11.3 Hz,), 4.49 (s, 4H, 4-H, 11-H), 6.80 (t, 1H, 20-H, ^4J = 1.9 Hz), 7.41 (t, 1H, 16-H, ^3J = 7.5 Hz), 7.57 (s, 4H, 7-H, 8-H, 18-H, 19-H), 7.98 (dd, 2H, 15-H, 17-H, ^3J = 7.5 Hz, $^4J'$ = 1.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 22.1 (3′-CH_{3eq}), 23.0 (3′-CH_{3ax}), 30.4 (3′-C), 72.0 (2′-C, 4′-C), 72.4 (4-C, 11-C), 101.4 (5-C, 10-C), 128.85 (16-C), 128.88 (7-C, 8-C, 18-C, 19-C), 130.5 (1-C, 14-C), 132.9 (20-C), 133.2 (15-C, 17-C), 137.6 (6-C, 9-C), 164.5 (2-C, 13-C); MS (EI, 70 eV) *m*/*z* 497 ([M + H]$^+$ 29), 453 (5), 208 (34), 149 (27), 104 (67), 69 (100). Anal. Calcd for $C_{28}H_{32}O_8$ (496.56): C, 67.74; H, 6.50. Found: C, 67.64; H, 6.68.

5,5;10,10;22,22;27,27-Tetrakis[3′,3′-dimethyl-1′,5′-dioxapentane-1′,5′-diyl]-2,13,19,30-tetraoxo-3,12,20,29-tetraoxapentacyclo[29.3.2^{6,9}.2^{23,26}.1^{14,18}.1^{1,31}]tetracontan-1(40),6,8,14,16,18(37),23(38),24,26(39),31,33-dodecaene (7b): white crystals; yield 18% (48 mg, 0.049 mmol); mp 350−351 °C; purified by flash chromatography (silica gel, diethyl ether/pentane = 2:3); R_f = 0.44; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.63 (s, 12H, 3′-CH_{3eq}), 1.24 (s, 12H, 3′-CH_{3ax}), 3.48 (d, 8H, 2′-H_{ax}, 4′-H_{ax}, ^2J = 10.9 Hz), 3.56 (d, 8H, 2′-H_{eq}, 4′-H_{eq}, ^2J = 10.9 Hz), 4.50 (s, 8H, 4-H, 11-H, 21-H, 28-H), 7.34 (t, 2H, 16-H, 33-H, ^3J = 7.5 Hz), 7.75 (s, 8H, 7-H, 8-H, 24-H, 25-H, 35-H, 36-H, 38-H, 39-H), 8.06 (d, 4H, 15-H, 17-H, 32-H, 34-H, ^3J = 7.5 Hz), 8.25 (s, 2H, 37-H, 40-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 22.0 (3′-CH_{3eq}), 22.9 (3′-CH_{3ax}), 30.4 (3′-C), 70.3 (4-C, 11-C, 21-C, 28-C), 71.7 (2′-C, 4′-C), 99.9 (5-C, 10-C, C-22, 27-C), 128.4 (16-C, 33-C), 128.7 (7-C, 8-C, 24-C, 25-C, 35-C, 36-C, 38-C, 39-C), 130.4 (1-C, 14-C, 18-C, 31-C), 130.9 (37-C, 40-C), 133.9 (15-C, 17-C, 32-C, 34-C), 137.3 (6-C, 9-C, 23-C, 26-C), 165.1 (2-C, 13-C, 19-C, 30-C); MALDI-TOF (*m*/*z*) 1015.2 [M + Na]$^+$, 1031.1 [M + K]$^+$. Anal. Calcd for $C_{56}H_{64}O_{16}$ (992.42): C, 67.73; H, 6.50. Found: C, 67.82; H, 6.71.

5,5;10,10;22,22;27,27;39,39;44,44-Hexakis[3′,3′-dimethyl-1′,5′-dioxapentane-1′,5′-diyl]-2,13,19,30,36,47-hexaoxo-3,12,20,29,37,46-hexaoxaheptacyclo[46.3.26,9.2^{23,26}.2^{40,43}.1^{14,18}.1^{31,35}.1^{1,48}]hexacontan-1(60),6,8,14,16,18(54),23(55),24,26(56),31,33,35(57),40(58),41,43(59),48,50,52-octadecaene (7c): white crystals; yield 2% (5 mg, 0.0036mmol); mp > 350 °C; purified by flash chromatography (silica gel, diethyl ether/pentane = 2:3); R_f = 0.13; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.57 (s, 18H, 3′-CH_{3eq}), 1.28 (s, 18H, 3′-CH_{3ax}), 3.46 (s, 24H, 2′-H_{ax}, 4′-$H_{ax,}$ 2′-H_{eq}, 4′-H_{eq}), 4.40 (s, 12H, 4-H, 11-H, 21-H, 28-H, 38-H, 45-H), 7.41 (t, 3H, 16-H, 33-H, 50-H, ^3J = 7.5 Hz), 7.62 (s, 12H, 7-H, 8-H, 24-H, 25-H, 41-H, 42-H, 52-H, 53-H, 55-H, 56-H, 58-H, 59-H), 8.12 (dd, 6H, 15-H, 17-H, 32-H, 34-H, 49-H, 51-H, ^3J = 7.5 Hz, ^4J = 1.5 Hz), 8.58 (t, 3H, 54-H, 57-H, 60-H, ^4J = 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 21.9 (3′-CH_{3eq}), 23.0 (3′-CH_{3ax}), 30.3 (3′-C), 70.4 (4-C, 11-C, 21-C, 28-C, 38-C, 45-C), 71.6 (2′-C, 4′-C), 99.8 (5-C, 10-C, 22-C, 27-C, 39-C, 44-C), 128.5 (16-C, 33-C, 50-C), 128.6 (7-C, 8-C, 24-C, 25-C, 41-C, 42-C, 52-C, 53-C 55-C, 56-C, 58-C, 59-C), 130.5 (1-C, 14-C, 18-C, 31-C, 35-C, 48-C), 131.1 (54-C, 57-C, 60-C), 134.0 (15-C, 17-C, 32-C, 34-C, 49-C, 51-C), 137.1 (6-C, 9-C, 23-C, 26-C, 40-C, 43-C), 165.1 (2-C, 13-C, 19-C, 30-C, 36-C, 47-C); MALDI-TOF (*m*/*z*) 1511.4 [M + Na]$^+$, 1527.4 [M + K]$^+$. Anal. Calcd for $C_{84}H_{96}O_{24}$ (1488,63): C, 67.73; H, 6.50. Found: C, 67.46; H, 6.59.

5,5;10,10;21,21;26,26-Tetrakis[3′,3′-dimethyl-1′,5′-dioxapentane-1′,5′-diyl]-2,13,18,29-tetraoxo-3,12,19,28-tetraoxapentacyclo[28.2.2^{6,9}.2^{14,17}.2^{22,25}.2^{1,30}]tetracontan-1(40),6,8,14,16,22(37),23,25(38),30(39),31,33,35-dodecaene (8b): white crystals; yield 19% (52 mg, 0.0515 mmol); mp = 240−241 °C; purified by flash chromatography (silica gel, diethyl ether/pentane = 1:1); R_f = 0.71; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.71 (s, 12H, 3′-CH_{3eq}), 1.25 (s, 12H, 3′-CH_{3ax}), 3.52 (s, 16H, 2′-H_{ax}, 4′-H_{ax},2′-H_{eq}, 4′-H_{eq}), 4.46 (s, 8H, 4-H, 11-H, 20-H, 27-H), 7.57 (s, 8H, 7-H, 8-H, 23-H, 24-H, 33-H, 34-H, 37-H, 38-H), 7.59 (s 8H, 15-H, 16-H, 31-H, 32-H, 35-H, 36-H, 39-H, 40-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 22.2 (3′-CH_{3eq}), 23.0 (3′-CH_{3ax}), 30.6 (3′-C), 70.2 (4-C, 11-C, 20-C, 27-C), 71.6 (2′-C, 4′-C), 99.1 (5-C, 10-C, C-21, 26-C), 128.1 (7-C, 8-C, 23-C, 24-C, 33-C, 34-C, 37-C, 38-C), 129.3 (15-C, 16-C, 31-C, 32-C, 35-C, 36-C, 39-C, 40-C), 133.4 (1-C, 14-C, 17-C, 30-C), 137.4 (6-C, 9-C, 22-C, 25-C), 164.7 (2-C, 13-C, 18-C, 29-C); SM

(IC, 200 eV) *m*/*z* 993 ([M + H]$^+$ 100). Anal. Calcd for $C_{56}H_{64}O_{16}$, (992.42): C, 67.73; H, 6.50. Found: C, 67.79; H, 6.37.

5,5;10,10;21,21;26,26;37,37;42,42-Hexakis[3′,3′-dimethyl-1′,5′-dioxapentane-1′,5′-diyl]-2,13,18,29,34,45-hexaoxo-3,12,19,28,35,44-hexaoxaheptacyclo[44. 2. 2^{6,9}.2^{14,17}.2^{22,25}.2^{30,33}.2^{38,41}.2^{1,46}]hexacontane-1(60),6,8,14,16,22,24,30,32,38(57),39,41(58),46(59),47,49,51,53,55-octadecaene (8c): white crystals; yield 14% (37 mg, 0.0252 mmol); mp = 243−244 °C; purified by flash chromatography (silica gel, diethyl ether/pentane = 1:1); R_f = 0.48; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.60 (s, 18H, 3′-CH_{3eq}), 1.27 (s, 18H, 3′-CH_{3ax}), 3.45 (s, 24H, 2′-H_{ax}, 4′-H_{ax}, 2′-H_{eq}, 4′-H_{eq}), 4.39 (s, 12H, 4-H, 11-H, 20-H, 27-H, 36-H, 43-H), 7.54 (s, 12H, 7-H, 8-H, 23-H, 24-H, 39-H, 40-H, 49-H, 50-H, 53-H, 54-H, 57-H, 58-H), 7.99 (s 12H, 15-H, 16-H, 31-H, 32-H, 47-H, 48-H, 51-H, 52-H, 55-H, 56-H, 59-H, 60-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 21.9 (3′-CH_{3eq}), 22.9 (3′-CH_{3ax}), 30.3 (3′-C), 70.3 (4-C, 11-C, 20-C, 27-C, 36-C, 43-C), 71.7 (2′-C, 4′-C), 99.6 (5-C, 10-C, C-21, 26-C, 37-C, 42-C), 128.5 (7-C, 8-C, 23-C, 24-C, 39-C, 40-C, 49-C, 50-C, 53-C, 54-C, 57-C, 58-C), 129.7 (15-C, 16-C, 31-C, 32-C, 47-C, 48-C, 51-C, 52-C, 55-C, 56-C, 59-C, 60-C), 133.9(1-C, 14-C, 17-C, 30-C, 33-C, 46-C), 137.1 (6-C, 9-C, 22-C, 25-C, 38-C, 41-C), 165.1 (2-C, 13-C, 18-C, 29-C, 34-C, 45-C); MALDI-TOF (*m*/*z*) 1511.5 [M + Na]$^+$, 1528.4 [M + K]$^+$. Anal. Calcd for $C_{84}H_{96}O_{24}$ (1488.63): C, 67.73; H, 6.50. Found: C, 67.84; H, 6.41.

5,5;10,10;21,21;26,26;37,37;42,42;53,53;58,58-Octakis[3′,3′-dimethyl-1′,5′-dioxapentane-1′,5′-diyl]-2,13,18,29,34,45,50,61-octaoxo-3,12,19,28,35,44,51,60-octaoxanonacyclo[60.2.2^{6,9}.2^{14,17}.2^{22,25}.2^{30,33}.2^{38,41}.2^{46,49}.2^{54,57}.2^{62,1}]octacontane-1(80),6,8,14,16,22,24,30,32,38(73),39,41(74),46(75),47,49(76),54(77),55,57(78),62(79),63,65,67,69,71-tetracosaene (8d): white crystals; yield 12% (32 mg, 0.0163 mmol); mp = 167−168 °C; purified by flash chromatography (silica gel, diethyl ether/pentane = 1:1); R_f = 0.35; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.60 (s, 24H, 3′-CH_{3eq}), 1.28 (s, 24H, 3′-CH_{3ax}), 3.46 (s, 32H, 2′-H_{ax}, 4′-H_{ax}, 2′-H_{eq}, 4′-H_{eq}), 4.37 (s, 16H, 4-H, 11-H, 20-H, 27-H, 36-H, 43-H, 52-H, 59-H), 7.55 (s, 16H, 7-H, 8-H, 23-H, 24-H, 39-H, 40-H, 55-H, 56-H, 65-H, 66-H, 69-H, 70-H, 73-H, 74-H, 77-H, 78-H), 8.02 (s 16H, 15-H, 16-H, 31-H, 32-H, 47-H, 48-H, 63-H, 64-H, 67-H, 68-H, 71-H, 72-H, 75-H, 76-H, 79-H, 80-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 21.9 (3′-CH_{3eq}), 22.9 (3′-CH_{3ax}), 30.4 (3′-C), 70.4 (4-C, 11-C, 20-C, 27-C, 36-C, 43-C, 52-C, 59-C), 71.7 (2′-C, 4′-C), 99.6 (5-C, 10-C, C-21, 26-C, 37-C, 42-C, 53-C, 58-C), 128.5 (7-C, 8-C, 23-C, 24-C, 39-C, 40-C, 55-C, 56-C, 65-C, 66-C, 69-C, 70-C, 73-C, 74-C, 77-C, 78-C), 129.7 (15-C, 16-C, 31-C, 32-C, 47-C, 48-C, 63-C, 64-C, 67-C, 68-C, 71-C, 72-C, 75-C, 76-C, 79-C, 80-C), 133.9 (1-C, 14-C, 17-C, 30-C, 33-C, 46-C, 49-C, 62-C), 137.2 (6-C, 9-C, 22-C, 25-C, 38-C, 41-C, 53-C, 57-C), 165.2 (2-C, 13-C, 18-C, 29-C, 34-C, 45-C, 50-C, 61-C); MALDI-TOF (*m*/*z*) 2008.7 [M + Na]$^+$, 2024.7 [M + K]$^+$. Anal. Calcd for $C_{112}H_{128}O_{32}$ (1984,84): C, 67.73; H, 6.50. Found: C, 67.89; H, 6.47.

5,5;10,10;21,21;26,26;37,37;42,42;53,53;58,58;69,69;74,74-Decakis[3′,3′-dimethyl-1′,5′-dioxapentane-1′,5′-diyl]-2,13,18,29,34,45,50,61,66,77-decaoxo-3,12,19,28,35,44,51,60,67,76-decaoxaundecacyclo[76.2.2^{6,9}.2^{14,17}.2^{22,25}.2^{30,33}.2^{38,41}.2^{46,49}.2^{54,57}.2^{62,65}.2^{70,73}.2^{78,1}]centane-1(100),6,8,14(83),15,17(84),22,24,30(87),31,33(88),38,40,46,48,54(93),55,57(94),62(95),63,65(96),70(97),71,73(98),78(99),79-hexacosaene (8e): white crystals; yield 9% (24 mg, 0.0097 mmol); mp = 141−142 °C; purified by flash chromatography (silica gel, diethyl ether/pentane = 1:1);, R_f = 0.28; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.60 (s, 30H, 3′-CH_{3eq}), 1.28 (s, 30H, 3′-CH_{3ax}), 3.47 (s, 40H, 2′-H_{ax}, 4′-H_{ax}, 2′-H_{eq}, 4′-H_{eq}), 4.38 (s, 20H, 4-H, 11-H, 20-H, 27-H, 36-H, 43-H, 52-H, 59-H, 68-H, 75-H), 7.56 (s, 20H, 7-H, 8-H, 23-H, 24-H, 39-H, 40-H, 55-H, 56-H, 71-H, 72-H, 81-H, 82-H, 85-H, 86-H, 93-H, 94-H, 97-H, 98-H), 8.05 (s 20H, 15-H, 16-H, 31-H, 32-H, 47-H, 48-H, 63-H, 64-H, 79-H, 80-H, 83-H, 84-H, 87-H, 88-H, 91-H, 92-H, 95-H, 96-H, 99-H, 100-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 21.9 (3′-CH_{3eq}), 22.9 (3′-CH_{3ax}), 30.3 (3′-C), 70.4 (4-C, 11-C, 20-C, 27-C, 36-C, 43-C, 52-C, 59-C, 68-C, 75-C), 71.7 (2′-C, 4′-C), 99.7 (5-C, 10-C, 21-C, 26-C, 37-C, 42-C, 53-C, 58-C, 69-C, 74-C), 128.6 (7-C, 8-C, 23-C, 24-C, 39-C, 40-C, 55-C, 56-C, 71-C, 72-C, 81-C, 82-C, 85-C, 86-C, 93-C, 94-C, 97-C, 98-C),129.7 15-C, 16-C, 31-C, 32-C, 47-C, 48-C, 63-C, 64-C, 79-C, 80-C, 83-C, 84-C, 87-C, 88-C, 91-C, 92-C, 95-C, 96-C, 99-C, 100-C), 133.9 (1-C, 14-C, 17-C, 30-C, 33-C, 46-C, 49-C, 62-C, 65-C, 78-C), 137.2 (6-C, 9-C, 22-C, 25-C, 38-C, 41-C, 54-C, 57-C, 69-C, 74-C), 165.2 (2-C, 13-C, 18-C, 29-C, 34-C, 45-C, 50-C, 61-C, 66-C, 77-C); MALDI-TOF (*m*/*z*) 2505.7 [M + Na]$^+$, 2521.5 [M + K]$^+$. Anal. Calcd for $C_{140}H_{160}O_{40}$ (2482.81): C, 67.73; H, 6.50. Found: C, 67.91; H, 6.68.

5,5;10,10-Bis[3′,3′-dimethyl-1′,5′-dioxapentan-1′,5′-diyl]-2,13-dioxo-20-aza-3,12-dioxatricyclo[12.3.2^{6,9}.1^{1,14}]icosan-1(20),6,8,14,16,18-hexaene (9a): white crystals; yield 46% (124 mg, 0.248 mmol); mp = 141−142 °C; purified by flash chromatography (silica gel, diethyl ether/pentane = 1:1); R_f = 0.42; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.70 (s, 6H, 3′-CH_{3eq}), 1.32 (s, 6H, 3′-CH_{3ax}), 3.52 (d, 4H, 2′-H_{ax}, 4′-H_{ax}, ^2J = 10.9 Hz), 3.73 (d, 4H, 2′-H_{eq}, 4′-H_{eq}, ^2J = 10.9 Hz), 4.60 (s, 4H, 4-H, 11-H), 7.48 (s, 4H, 7-H, 8-H, 18-H, 19-H), 7.87 (t, 1H, 16-H, ^3J = 7.5 Hz), 8.08 (d, 2H, 15-H, 17-H, ^3J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 22.1 (3′-CH_{3eq}), 23.1 (3′-CH_{3ax}), 30.5 (3′-C), 72.04 (2′-C, 4′-C), 72.14 (4-C, 11-C), 101.8 (5-C, 10-C), 127.1 (16-C), 128.8 (7-C, 8-C, 18-C, 19-C), 136.9 (6-C, 9-C), 138.0 (15-C, 17-C), 147.6 (1-C, 14-C), 163.4 (2-C, 13-C); SM (FAB) (*m*/*z*) 498 [M + H]$^+$. Anal. Calcd for $C_{27}H_{31}NO_8$ (497.55): C, 65.18; H, 6.28; N, 2.82. Found: C, 65.52; H, 6.58; N, 2.61.

Acknowledgment. We acknowledge the financial support of this work by UEFISCSU (projects ET/2006 and ID-18/2007) and by the CEEX-program (project 2Cex06-11-50).

Supporting Information Available: Structures of synthesized cyclophanes, details of the inter- and intramolecular interactions in solid state, details of ^{1}H NMR spectra, NOESY spectrum of compound **7a**, copies of ^{1}H and ^{13}C NMR spectra, CIF files, and a table of parameters for the crystallographic determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

JO8006489