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Cyclic Tetra- and Hexaynes Containing 1,4-Donor-Substituted Butadiyne Units: Synthesis and Supramolecular Organization

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Cyclic bis(1,3-butadiynes) with sulfur centers placed in the α-position to the 1,3-butadiyne units (**2(n)**) were synthesized by Glaser coupling of the corresponding open chain dithia-α,ω-diynes **1-(n)**. In a second protocol we applied a four-component cyclization by reacting α,ω-dithiocyanatoalkanes **6(n)** or α,ω-diselenocyanatoalkanes **7(n)** with dilithium-1,3-butadiynide. This concept afforded either the cyclic dimers (S, **2(n)**; Se, **9(n)**) or the cyclic trimers (S, **8(n)**; Se, **10(n)**). Most of the molecular structures of **2(n)** and **9(n)** adopt chairlike conformations in the solid state. Tubular structures in the solid state with short distances between the chalcogen centers of neighboring stacks were encountered for **2(5)**, **9(5)**, **8(4)**, **10(4)**, and **10(5)**. Recrystallization of **10(5)** from various polar and nonpolar solvents yielded inclusion of the solvent guest molecules. The solvent-accessible volume was calculated to vary from 19% (*n*-hexane) to 25% (mesitylene). The elastic properties of our cycles are due to the flexible methylene chains and the easily variable torsional angles between the rigid 1,3-butadiyne rods.

Introduction

For a long time, the design of microporous organic solids has been a fascinating and rewarding but also a difficult goal to reach. Due to the isotropic nature of weak intermolecular interactions, most compounds show closest-packing in the solid state.[1] By using more directional forces such as hydrogen bonding[2] or interactions between Lewis acidic metal centers and bases[3,4] chemists succeeded in building porous networks[5] and channel-like structures.[6] In many cases, interpenetrating networks[7] are formed in order to minimize the empty space between the coordination polymers, which was in earlier times referred to as Nature's *horror vacui*. Another impressive approach to building cavities was to use large shape-persistent molecular entities that are stacked on top of each other by $\pi-\pi$ interactions.[8,9] All these concepts can also be combined with each other to afford a useful tool kit for crystal engineering[10] as well as for biomimetic chemistry.[11]

Recently, we investigated a large variety of chalcogen-containing compounds, which pile up to build columnar or even tubular stacks.[12] Common to all of them are close chalcogen−chalcogen contacts in the solid state. The corresponding structure-determining interactions can be rationalized in terms of frontier orbital theory. Lone pairs at the heteroatoms interact with low-lying unoccupied σ^* orbitals.[13,14] Furthermore, electron correlation and dispersion effects contribute significantly.[14,15] Hitherto, the diameters of the tunnels provided by the columnar

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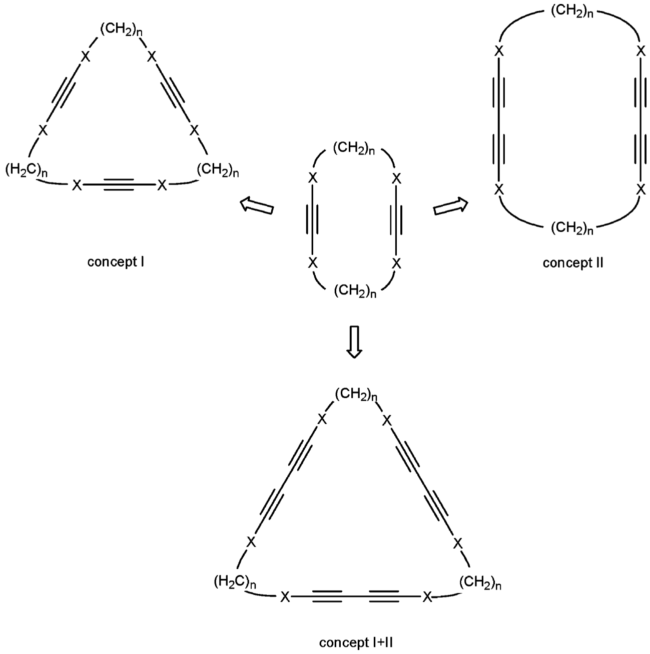
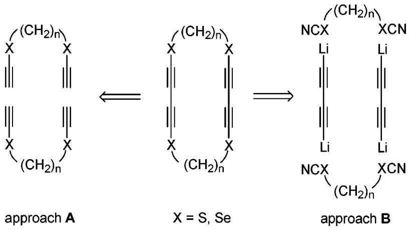
10.1021/jo035882+ CCC: $27.50

SCHEME 1

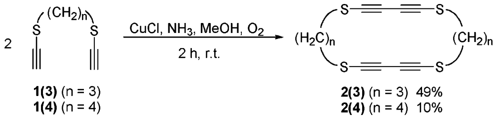


structures are too small for the inclusion of guest molecules. To provide enough space we built up larger cycles, which result in larger cavities. There are at least two different concepts (Scheme 1) to achieve this goal: The first is a further repetition of the rigid donor-substituted alkyne moiety to afford cyclic triynes and tetraynes (concept I).

SCHEME 2



SCHEME 3



But as some of our previous results have shown, these systems are too flexible, especially when the bridging alkane chains become longer. The second concept is a simple elongation of the rigid unit by introducing a second triple bond to get a 1,4-donor-substituted 1,3-butadiyne unit (concept II). Of course, the best results are expected by a combination of the two concepts: to take more rigid units and to elongate them (concepts I + II).

Herein, we report our systematic in-depth studies of tubular structures that have been obtained by self-assembly of tetra- and hexaynes favored by close chalcogen–chalcogen interactions.

Results and Discussion

Syntheses. To achieve our goals, the synthesis of macrocyclic donor-substituted tetra- and hexaynes, we envisaged the two possibilities shown in Scheme 2. One reasonable protocol starts with the recently described dithiaalkadiynes[16] (approach A in Scheme 2), which can be coupled at the terminal sp centers. Another path (approach B) uses a four-component cyclization between two lithiated 1,3-butadiyne units and functionalized alkanes at their termini.

In Scheme 3, we summarize the results of the dimerization of the dithiaalkadiynes **1(3)** and **1(4)**. These were dimerized under Glaser conditions in methanol as a solvent. After addition of the copper solution to the diynes, an immediate color change was observed. Hence, we assume a reaction occurred between the copper cations and the sulfur centers of the organic fragment. Similar compounds without sulfur centers have not shown such a behavior. Nevertheless, the desired coupling products **2(3)** and **2(4)** (Scheme 3) were obtained in 49 and 10% yields, respectively. In contrast, a trimerization of the diyne could not be observed.

Instead, in the reaction of **1(4)** under Glaser conditions, **4** (Scheme 4) was obtained as a side product in 10% yield. To rationalize the origin of this compound, we assume that an intramolecular cyclization took place to afford the highly strained 10-membered butadiyne derivative **3** (Scheme 4).[17] Quantum chemical model calculations (B3LYP/6-311G*)[18,19] on the intermediate **3** have shown that the angles at the acetylenic carbon atoms deviate

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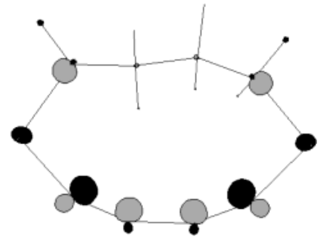
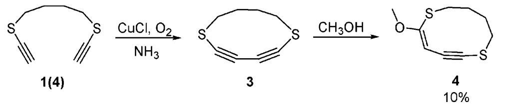
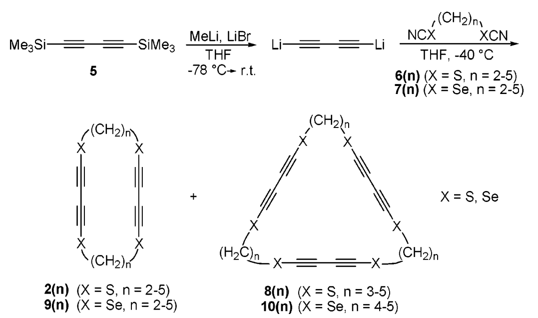


FIGURE 1. Schematic representation of the LUMO of the highly strained 10-membered butadiyne **3**.

SCHEME 4



SCHEME 5



between 22 and 27° from linearity. Considering HF calculations, this strain corresponds to a decrease of the LUMO energy (by 0.7 eV) compared to the unstrained congener.[20] Even the regioselectivity of the attack is obvious by considering the corresponding coefficients of the LUMO. As Figure 1 shows, the large coefficients at the acetylenic carbons next to the sulfur favor the attack of the highly nucleophilic MeOH at this position. As a consequence, the enyne **4** was observed as the only regioisomer. Its structure was confirmed by X-ray crystallography.

Our experiments reveal no evidence for a trimerization of **1** to yield cyclohexaynes as indicated in Scheme 1. Therefore, we tried approach B (Scheme 2). In this endeavor, we made use of a protocol related to that recently applied for the synthesis of sulfur- and selenium-capped carbon rods.[20] The rather stable trimethylsilyl-substituted butadiyne **5** was deprotected in THF at −78 °C by methyllithium in the presence of lithium bromide (Scheme 5). The bis(lithium) salt was treated at −40 °C with dithio- and diselenocyanatoalkanes **6(n)** and **7(n)**, respectively, applying high-dilution conditions. The advantage of this approach was that also the six-component products, the cyclohexaynes **8(n)** and **10(n)**, were obtained in most cases (Scheme 5). The tetraynes **2(n)** and **9(n)** can be easily separated from the hexaynes and several other oligomeric products by column chromatography. The yields of the tetra- and hexaynes are reported in Table 1. The resulting compounds proved to be air-stable, slightly light-sensitive, colorless to yellow solids. Some of them do explode on heating.

TABLE 1. Yields of 2(n) and 8(n)−10(n) in the Multicomponent Cyclization as a Function of *n*

compd	$n = 2$	$n = 3$	$n = 4$	$n = 5$
2(n)	4	17	18	11
8(n)		9	6	6
compd	$n = 2$	$n = 3$	$n = 4$	$n = 5$
9(n)	2	5	17	4
10(n)			3	3

Structural Investigations. (a) Molecular Structures. For all new compounds we were able to grow single crystals suitable for X-ray investigations. As examples, we show in Figure 2 the molecular structures of four tetraynes **2(2)**, **2(3)**, **9(4)**, and **9(5)**. With the exception of **2(2)** and **2(4)**, all tetraynes show a center of inversion. In Table 2, we list the most relevant distances, angles, and torsional angles of the tetraynes **2(n)** and **9(n)** found in the solid state.

These are four transannular distances $t_1 - t_4$ as well as the angles describing the bending of the triple bonds ($\alpha_1 - \alpha_8$) and the torsional angles (β, γ_1, and γ_2) as defined in Figure 3. Not compiled in Table 2 are the lengths of the triple bonds as well as the distances between the sp centers and the chalcogen atoms. The former modulate between 118 and 121 pm, values that were also encountered for cyclic mono- and diynes.[21] The latter vary between 166 and 169 pm for the sulfur congeners and between 182 and 184 pm for the selenium congeners, respectively. The distances between opposite triple bonds ($t_1 - t_4$) spread from 431 to 821 pm. This diversity was anticipated insofar as longer chains imply larger separations. Due to symmetry the values of the pairs t_1/t_4, t_2/t_3, α_1/α_4, α_2/α_3, α_5/α_8, and α_6/α_7 are very similar. Therefore, we have listed in Table 2 only their mean values. The angles $\alpha_1 - \alpha_8$ vary only slightly between 174 and 180 pm, indicating that the donor-substituted butadiyne unit is usually a straight building block and the cycles are strain-free. In most cases, the torsional angle β between the butadiyne units was found to be 0° showing that some kind of chairlike conformation is adopted. A comparison among the torsional angles γ_1 and γ_2 between the CH_2−X σ-bonds shows a large variety of different values from 0 to 88°.

In contrast, the conformations of these cycles are not mainly determined by electronic effects as observed in cyclic tetrathia-[16] and tetraselenadiynes[12a] where only one triple bond links the chalcogen centers. The longer distance spanned by two acetylene units reduces the repulsive interactions between the lone pairs of the heteroatoms remarkably. The favored perpendicular conformation is circumvented by steric or packing effects. Recent quantum chemical calculations confirm this view.[20] They show that the rotational barriers of the correspond-

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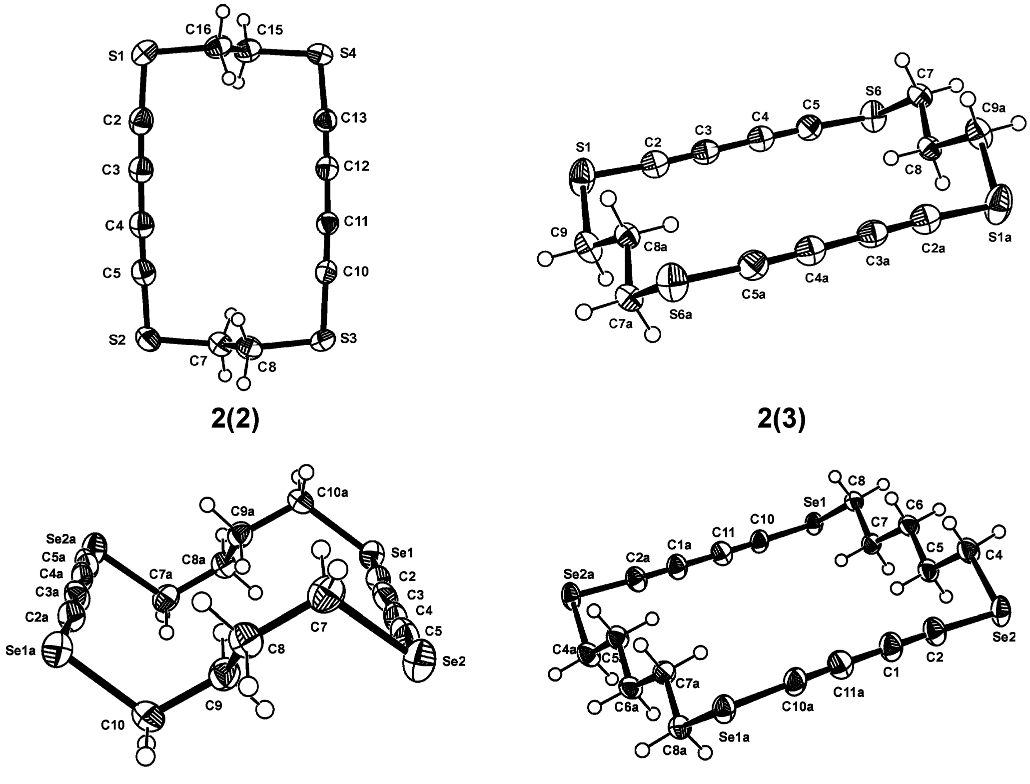

2(2) **2(3)**

9(4) **9(5)**

FIGURE 2. ORTEP plots (50% ellipsoid probability) of the molecular structures of **2(2)**, **2(3)**, **9(4)**, and **9(5)**.

TABLE 2. Most Relevant Distances, Angles, and Torsional Angles of the Cyclotetraynes 2(n) and 9(n)

compd	$(t_1 + t_4)/2$ [pm]	$(t_2 + t_3)/2$ [pm]	$(\alpha_1 + \alpha_4)/2$ [deg]	$(\alpha_2 + \alpha_3)/2$ [deg]	$(\alpha_5 + \alpha_8)/2$ [deg]	$(\alpha_6 + \alpha_7)/2$ [deg]	β [deg]	γ_1 [deg]	γ_2 [deg]
2(2)[a]	457	462	177	178	178	179	13	13	14
	435	431	177	178	177	178	0	0	0
2(3)	544	547	176	180	176	180	0	64	64
2(4)	544	535	176	178	177	176	36	76	88
2(5)α	804	804	179	178	179	178	0	63	63
2(5)β	813	821	178	177	179	178	0	62	62
9(2)	460	458	176	177	176	177	0	0	0
9(3)	559	558	178	179	178	179	0	69	69
9(4)	615	614	178	178	177	178	0	0	0
9(5)	814	810	178	179	178	179	0	60	60

[a] Asymmetric unit contained 1.5 independent molecules.

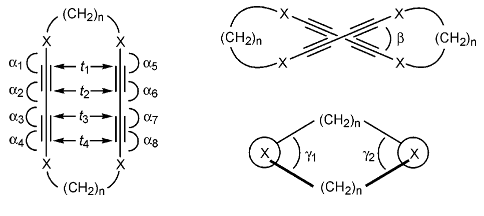

FIGURE 3. Definitions of transannular distances t_1–t_4, angles α_1–α_8, and torsional angles β, γ_1, and γ_2 in **2(n)** and **9(n)**.

ing butadiyne systems are only about 50% of the monoacetylenic ones.[20]

A systematic discussion of the hexaynes **8(n)** and **10(n)** concerning their molecular structures is not meaningful. The structures are determined by the three rigid donor-substituted butadiyne units. The three bridging alkane chains try to adopt energetically favored zigzag conformations. As a result, some kind of elastic cycle is obtained containing stiff and rather flexible units.

(b) Self-Assembly and Packing in Crystal. As previously mentioned, in many cases, close chalcogen–chalcogen contacts are responsible for the occurrence of columnar or even tubular stacks.[12] Concerning the tetraynes, we noticed the appearance of channel-like structures in the solid state in the case of **2(5)** and **9(5)**. The structures themselves are very similar to that of the cyclic tetrathia- and tetraselenadiynes, respectively.[12a,c] Due to the butadiyne unit, the rectangular cavity is enlarged, and the chalcogen atoms are located at the four edges of the rather flat rectangle. In the solid state, the cycles associate in such a way that the chalcogen centers of one cycle keep in close contact with chalcogen centers of neighboring rings. As a result, a channel-like structure arises. By recrystallizing **2(5)** from *n*-hexane, we found no solvent molecules in these cavities (modification α).

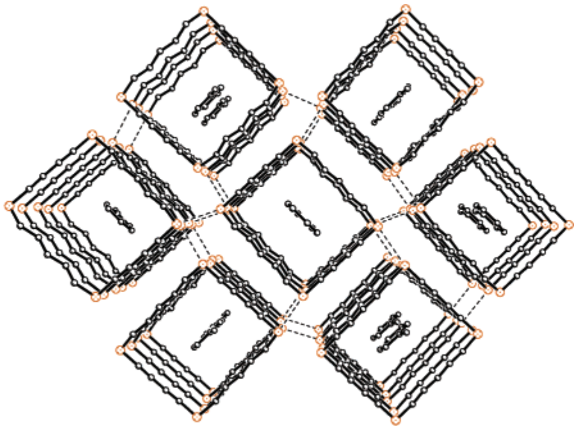

FIGURE 4. Columnar structure of **2(5)** in the solid state with included toluene guest molecules. H atoms are omitted for the sake of clarity.

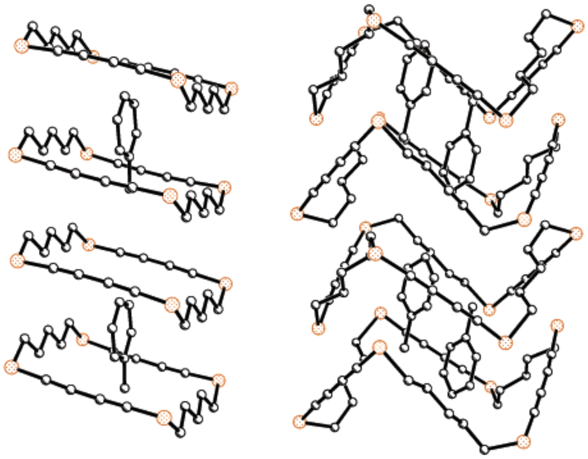

FIGURE 5. Side views showing the stacking of the rings of **2(5)** (left) and **10(5)** (right), both with included toluene guest molecules. The H atoms are omitted for the sake of clarity.

In contrast, by using toluene we observed the inclusion of one aromatic molecule per two cyclotetrayne molecules in a regular manner (modification *β*) as shown in Figure 4 (top view) and Figure 5 (left, side view).

Calculations of the solvent-accessible volume carried out with the PLATON program[22] revealed that 13.1% (α) and 16.1% (*β*), respectively, of the crystal volume may be occupied by solvent. Similar experiments with **9(5)** afforded an analogous solid-state structure, including *n*-hexane as guest, which could only be detected as disordered electron density.

By recrystallizing the hexathiacyclohexayne with bridging butano moieties **8(4)** from *n*-hexane, we observed a columnar stacking. But due to the small angle between the stacking axis and the plane of the macrocycle, the potential cavity was too small for the inclusion of guests (modification α). In contrast, when toluene was used as the solvent we obtained a channel-like structure with two independent molecules of the macrocycle and an ABCD stacking. Inside the tubes, slightly disordered toluene molecules were observed (modification *β*).

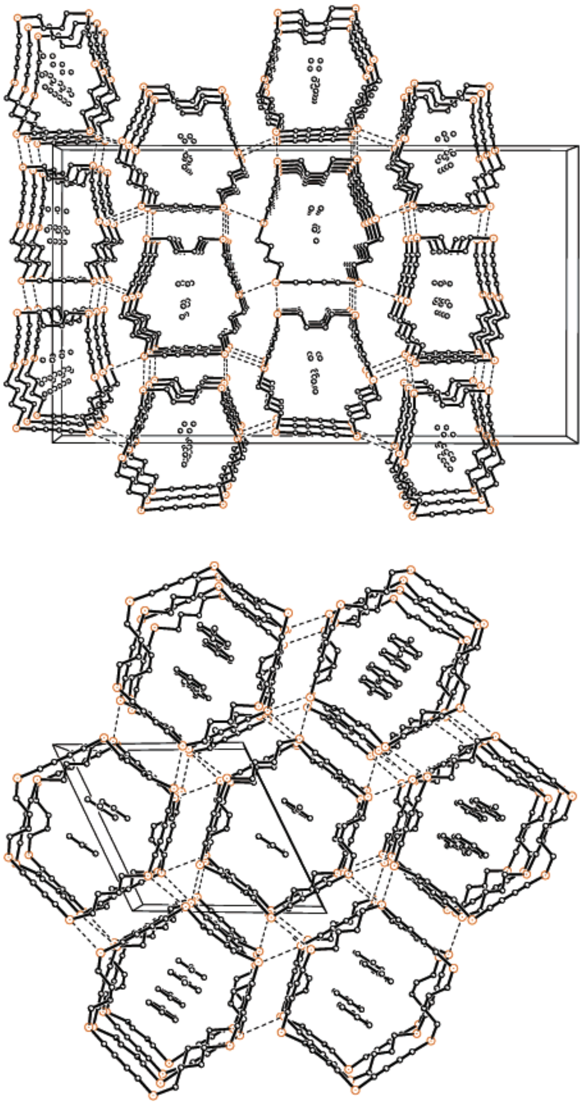

FIGURE 6. Top view of two totally different modifications of **10(4)**: (top) with included disordered *n*-hexane molecules, (bottom) with included toluene molecules. Short Se···Se contacts are indicated as well as the unit cell dimensions. H atoms are omitted for the sake of clarity.

For the selenium congener **10(4)**, two different kinds of supramolecular organizations are shown in Figure 6. In the first case, disordered *n*-hexane molecules are incorporated, and AAA stacking of the molecules is observed (modification α). In the second case showing an ABAB stacking, toluene guest molecules are accommodated at well-defined positions (modification *β*). Here, by contrast with the smaller cycle **2(5)**, one molecule of the aromatic guest per macrocycle is included (Figure 6, bottom). Calculations of the solvent-accessible volume[22] revealed values of 19.2% for α and 24.3% for *β*, respectively. These two modifications show extremely short intermolecular Se···Se distances between two neighboring stacks of molecules (α, 360 and 378 pm; *β*, 366 and 368 pm). These distances are much shorter than the sum of the van der Waals radii (400 pm).[23] Examining the directionality of these interactions shows that the 4p lone

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TABLE 3. Systematic Study of the Solid-State Behavior of 10(5) Depending on the Included Guest Molecules

structure	guest molecule	crystal system	volume [%][a]	angle ϕ [deg][b]	angle ψ [deg][c]
10(5)α	furane	trigonal	18.9	37.8	nd
10(5)β	*n*-hexane	trigonal	19.2	37.6	nd
10(5)γ	thiophene	trigonal	20.0	36.6	nd
10(5)δ	benzene	trigonal	20.3	36.1	90/nd
10(5)ϵ	aniline	trigonal	20.4	36.0	nd
10(5)ζ	chlorobenzene	trigonal	20.7	35.9	20
10(5)η	nitrobenzene	triclinic	20.8	35.5	32
10(5)θ	toluene	triclinic	20.8	35.3	12
10(5)ι	anisole	triclinic	21.0	35.1	9
10(5)κ	*p*-xylene	triclinic	23.3	34.1	1
10(5)λ	4-bromoanisole	triclinic	23.5	33.6	16
10(5)μ	mesitylene	triclinic	25.6	30.6	1

[a] Solvent-accessible volume of the unit cell, calculated with PLATON.[22] [b] Angle ϕ between the medium plane of the macrocycle and the SeC_4Se unit(s). [c] Angle ψ between the tubular axis and the aromatic plane of the guest molecule.

pairs at the Se centers directly coincide with the directions of the Se−C σ^* orbitals of the neighboring cycles.

In the case of hexaselenacyclohexayne **10(5)**, we carried out a systematic study in order to examine the solid-state behavior dependent on the kind of guest molecule included. The results of this study are shown in Table 3. In total, 12 different guest molecules were included, aliphatic as well as aromatic, and electron-rich as well as electron-poor ones. All structures have very similar primitive unit cells, some of them leading to a higher symmetric R-centered lattice. Each structure is described by a greek letter (from α to μ). In the cases, when the trigonal space group $R\bar{3}$ was observed, the guest molecules could not be localized at well-defined positions. In the other cases, when the guests were found on well-defined positions, the trigonal symmetry of the crystal was not present and a triclinic space group resulted ($P\bar{1}$). The fact that many solvent molecules are incorporated in an ordered fashion can be ascribed to weak C−H···π interactions[2,24] between the alkane chains of the macrocycle and the π system of the aromatic guest. Furthermore, we list in Table 3 also the solvent-accessible volume calculated with the PLATON program,[22] the angle ϕ between the medium plane of the macrocycle and the SeC_4Se unit(s), and the angle ψ between the tubular axis and the aromatic plane of the guest molecule. The latter values differ considerably, so we abstain from a discussion.

Table 3 unambiguously illustrates that the diameter of the tubes, and therefore the solvent-accessible volume of the crystal, is easily controllable by the kind of guest molecule used. The larger the guest, the more the tubes are stretched. Furthermore, a straightforward correlation between the solvent-accessible volume and the angle ϕ is observed: the smaller ϕ, the larger the solvent-accessible volume. Thus, neither a potential bending of the butadiynyl fragments nor a contribution of the saturated alkyl linkers is responsible for the increased cavity size. The most important factor is the variation of the torsional angle ϕ at the donor-substituted butadiyne unit serving as a hinge.

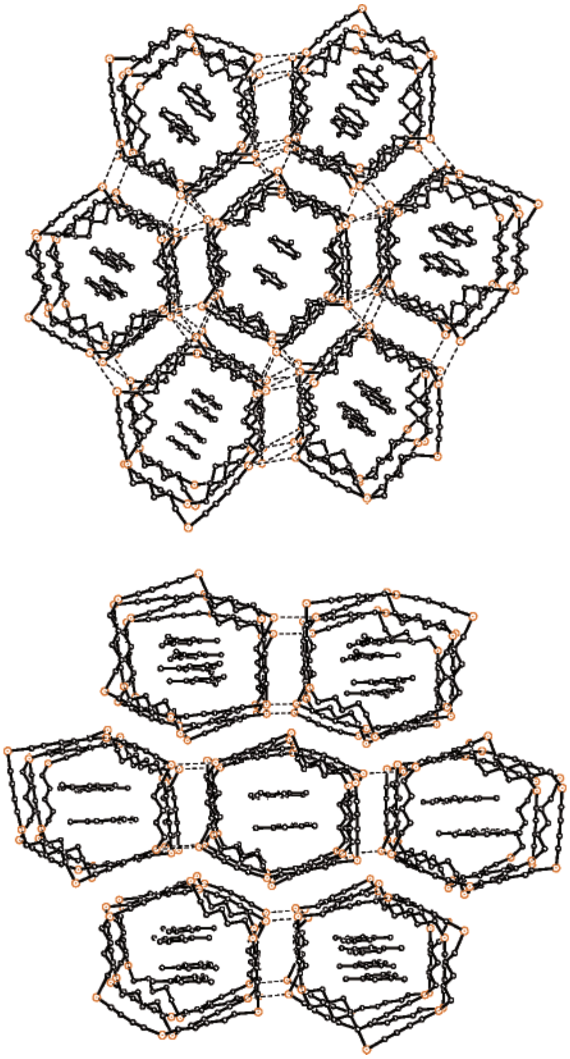

FIGURE 7. Top view of **10(5)**: (top) with included toluene molecules, (bottom) with included mesitylene molecules showing a structure with larger cavities. Short Se···Se contacts are indicated. The H atoms are omitted for the sake of clarity.

Figure 7 compares the shapes of the solid-state structures of **10(5)** containing toluene and mesitylene. In the former, the solvent-accessible volume[22] is 20.8% of the volume of the unit cell, whereas in the latter this value amounts to 25.6%. The more voluminous guest mesitylene with the two additional methyl groups affords an increase in the channel diameter. In crystallographic parameters, this means a decrease of the axis in stacking direction (short axis) by 2.3%, whereas the two longer axes of the unit cell increase by 3.2%. As a result, the solvent-accessible volume increases by 23% compared with the toluene-containing structure. In contrast, occupying the channels with a sea of highly disordered *n*-hexane molecules that are totally flexible decreases the value for the solvent-accessible volume to 19.2%. With the sulfur congener **8(4)**, we have carried out similar experiments with *n*-hexane and toluene, respectively, showing quasi-isomorphous structures.

To differentiate the special behavior of our cycles from the well-known shape-persistent macrocycles[8,9] on one hand and from the rather flexible rings on the other, we suggest the term "elastic cycle".

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Conclusion

The columnar structures we discovered during our studies of chalcogen-containing macrocycles led us to design pathways to afford large rings with rigid 1,4-dichalcogeno-1,3-butadiynes connected with *n*-alkane bridges. This endeavor was undertaken to use the columns as hosts. The first approach we used was the Glaser coupling of two α,ω-dithiadiyne. This led to the tetrathiatetraynes **2(n)** with $n = 3$ and 4, only. Since this approach proved to be rather limited, we used a four-component cyclization to prepare rings with two and three 1,4-dichalcogeno-1,3-butadiynes such as **2(n)** and **8(n)**−**10(n)** with $n = 2-5$. These two methods provided rings consisting of rigid and flexible building units. Although the yields of the cycles were small, enough material was produced to carry out further studies. The most interesting outcome was the elasticity of the resulting columns of **8(4)**, **10(4)**, and **10(5)**, which can be traced back to the intrinsic flexibility of the rings. To the best of our knowledge, the columnar structures known so far, built of macrocycles, lack such an elasticity. In the long term, we consider placing a polymerizable group at the cycles' periphery in order to covalently freeze in the tubular stacks.

Experimental Section

General Methods. All reactions were conducted in oven-dried glassware under an argon atmosphere with magnetic stirring. THF was dried with sodium/benzophenone and distilled under argon before use. Melting points are uncorrected. Materials used for column chromatography: silica gel 60. ^{1}H NMR and ^{13}C NMR were recorded either at 300 and 500 MHz (^{1}H NMR) or 75.5 and 125.8 MHz (^{13}C NMR) using the solvent as an internal standard. The IR spectra were recorded with a FT-IR instrument. The high-resolution mass spectra (HRMS) were recorded in the EI (70 eV) mode and in the positive ion FAB mode in *m*-nitrobenzyl alcohol. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. Dithiocyanatoalkanes **6(n)**,[25] diselenocyanatoalkanes **7(n)**,[26] dithiadiynes **1(n)**,[16] and bis(trimethylsilyl)butadiyne **5**[27] were prepared according to literature methods.

General Procedure for the Preparation of the Cyclic Tetraynes and Hexaynes. To a solution of bis(trimethyl)-butadiyne (**5**) in THF was added MeLi/LiBr in diethyl ether (1.5 M) dropwise at −78 °C over a period of 20 min. The solution was stirred for 3 h at −78 °C. The resulting suspension of dilithium butadiynide in THF and a solution of the corresponding dithiocyanatoalkane **6(n)** and diselenocyanatoalkane **7(n)**, respectively, in THF were added dropwise simultaneously at −40 °C over a period of 4 h to 500 mL of anhydrous THF. After complete addition, the reaction mixture was allowed to warm to room-temperature overnight. The solvent was removed by rotary evaporation. Polymers and salts were removed by flash filtration (SiO_2 with 3%(v/v) NEt_3, toluene as the eluent). The solvent was removed by rotary evaporation. Column chromatography of the crude product (SiO_2, *n*-hexane/diethyl ether or *n*-hexane/dichloromethane as the eluent) afforded the cyclic tetrayne and in most cases the cyclic hexayne.

1,6,9,14-Tetrathiacyclohexadeca-2,4,10,12-tetrayne (2(2)). Starting materials: 2.53 g (13.0 mmol) of **5**, 20.0 mL (30.0 mmol) of MeLi/LiBr in diethyl ether, and 2.02 g (14.0 mmol) of 1,2-dithiocyanatoethane (**6(2)**). Column chromatography afforded 78 mg (4.3%) of **2(2)** as a colorless solid: mp 85 °C (dec); ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 3.19 (s, 8H, SCH_2); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 37.1 (SCH_2), 73.2 (SCC), 81.4 (SCC); IR (KBr) 2922, 2852, 2079, 1629, 1414 cm^{-1}; MS (EI, 70 eV) 280 [M^{+}], 252, 124, 112; HRMS (EI, 70 eV) calcd for $C_{12}H_8S_4$ 279.9508, found 279.9550.

1,6,10,15-Tetrathiacyclooctadeca-2,4,11,13-tetrayne (2(3) and 1,6,10,15,19,24-Hexathiacycloheptacosa-2,4,11,13,20,-22-hexayne (8(3)). Starting materials: 2.53 g (13.0 mmol) of **5**, 20.0 mL (30.0 mmol) of MeLi/LiBr in diethyl ether, and 2.21 g (14.0 mmol) of 1,3-dithiocyanatopropane (**6(3)**). Column chromatography afforded 385 mg (17.2%) of **7(3)** and 183 mg (9.1%) of **8(3)** as colorless solids.

2(3): mp 157 °C (explosion); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.35 (quint, $^{3}J = 7.1$ Hz, 4H, SCH_2CH_2), 2.76 (t, $^{3}J = 7.1$ Hz, 8H, SCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.5 (SCH_2CH_2), 33.7 (SCH_2), 73.1 (SCC), 81.8 (SCC); IR (KBr) 2919, 2075, 1629, 1444 cm^{-1}; MS (EI, 70 eV) 308 [M^{+}], 190, 112; HRMS (EI, 70 eV) calcd for $C_{14}H_{12}S_4$ 307.9822, found 307.9817.

8(3): mp 145 °C (dec); ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 2.27 (quint, $^{3}J = 7.0$ Hz, 6H, SCH_2CH_2), 2.88 (t, $^{3}J = 7.1$ Hz, 12H, SCH_2); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 29.7 (SCH_2CH_2), 34.2 (SCH_2), 73.6 (SCC), 81.3 (SCC); IR (KBr) 2921, 2070, 1634, 1438 cm^{-1}; MS (FD) 462 [M^{+}].

1,6,11,16-Tetrathiacyclooeicosa-2,4,12,14-tetrayne (2(4)) and 1,6,11,16,21,26-Hexathiacyclotriaconta-2,4,12,14,22,-24-hexayne (8(4)). Starting materials: 2.53 g (13.0 mmol) of **5**, 20.0 mL (30.0 mmol) of MeLi/LiBr in diethyl ether, and 2.41 g (14.0 mmol) of 1,4-dithiocyanatobutane (**6(4)**). Column chromatography afforded 403 mg (18.4%) of **2(4)** and 128 mg (5.9%) of **8(4)** as colorless solids.

2(4): mp 113 °C; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 1.96 (m, 8H, SCH_2CH_2), 2.77 (m, 8H, SCH_2); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 28.4 (SCH_2CH_2), 35.8 (SCH_2), 73.3 (SCC), 81.4 (SCC); IR (KBr) 2936, 2075, 1634, 1450 cm^{-1}; MS (EI, 70 eV) 336 [M^{+}], 250, 204, 112; HRMS (EI, 70 eV) calcd for $C_{16}H_{16}S_4$ 336.0135, found 336.0125. Anal. Calcd for $C_{16}H_{16}S_4$: C, 57.10; H, 4.79; S, 38.11. Found: C, 57.24; H, 4.79; S, 38.17.

8(4): mp 133 °C (dec); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.94 (m, 12H, SCH_2CH_2), 2.78 (m, 12H, SCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.9 (SCH_2CH_2), 35.2 (SCH_2), 73.4 (SCC), 81.4 (SCC); IR (KBr) 2932, 2073, 1627, 1445 cm^{-1}; MS (FD) 504 [M^{+}]. Anal. Calcd for $C_{24}H_{24}S_6$: C, 57.10; H, 4.79; S, 38.11. Found: C, 57.07; H, 4.89; S, 38.30.

1,6,12,17-Tetrathiacyclodocosa-2,4,13,15-tetrayne (2(5)) and 1,6,12,17,23,28-Hexathiacyclotritriaconta-2,4,13,15,-24,26-hexayne (8(5)). Starting materials: 2.53 g (13.0 mmol) of **5**, 20.0 mL (30.0 mmol) of MeLi/LiBr in diethyl ether, and 2.70 g (14.5 mmol) of 1,5-dithiocyanatopentane (**5(5)**). Column chromatography afforded 250 mg (10.5%) of **7(5)** and 135 mg (5.7%) of **8(5)** as colorless solids.

2(5): mp 155 °C (dec); ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 1.54 (m, 4H, $SCH_2CH_2CH_2$), 1.87 (m, 8H, SCH_2CH_2), 2.68 (t, $^{3}J = 7.4$ Hz, 8H, SCH_2); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 27.5 ($SCH_2CH_2CH_2$), 29.7 (SCH_2CH_2), 35.4 (SCH_2), 73.1 (SCC), 81.4 (SCC); IR (KBr) 2935, 2856, 2072, 1627 cm^{-1}; MS (EI, 70 eV) 364 [M^{+}], 281, 262, 112; HRMS (EI, 70 eV) calcd for $C_{18}H_{20}S_4$ 364.0448, found 364.0463.

8(5): mp 76 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.59 (quint, $^{3}J = 6.8$ Hz, 6H, $SCH_2CH_2CH_2$), 1.84 (pquint, 12H, SCH_2CH_2), 2.75 (t, $^{3}J = 7.1$ Hz, 12H, SCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.8 ($SCH_2CH_2CH_2$), 29.0 (SCH_2CH_2), 35.7 (SCH_2), 73.6 (SCC), 81.2 (SCC); IR (KBr) 2930, 2853, 2074,1637 cm^{-1}; HRMS (FAB) calcd for $C_{27}H_{31}S_6$ 547.0750, found 547.0714. Anal. Calcd for $C_{27}H_{30}S_6 \cdot 0.3C_6H_{14}$: C, 60.40; H, 6.02. Found: C, 60.31; H, 6.15.

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1,6,9,14-Tetraselenacyclohexadeca-2,4,10,12-tetrayne (9(2)). Starting materials: 2.17 g (11.2 mmol) of **5**, 17.2 mL (25.7 mmol) of MeLi/LiBr in diethyl ether, and 3.00 g (12.4 mmol) of 1,2-diselenocyanatoethane (**7(2)**). Column chromatography afforded 44 mg (1.7%) of **9(2)** as a slightly brown solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 3.30 (s, 8H, SeCH_2); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 31.2 (SeCH$_2$), 65.6 (SeCC), 84.9 (SeCC); IR (KBr) 2923, 2067, 1628, 1412 cm^{-1}; MS (FD+) 468 [M$^+$].

1,6,10,15-Tetraselenacyclooctadeca-2,4,11,13-tetrayne (9(3)). Starting materials: 2.53 g (13.0 mmol) of **5**, 20.0 mL (30.0 mmol) of MeLi/LiBr in diethyl ether, and 3.60 g (14.5 mmol) of 1,3-diselenocyanatopropane (**7(3)**). Column chromatography afforded 174 mg (5.4%) of **9(3)** as a slightly brown solid: mp 155 °C (dec); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.25 (quint, ^3J = 7.5 Hz, 4H, SeCH$_2$CH_2), 2.89 (t, ^3J = 7.5 Hz, 8H, SeCH_2); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 28.1 (SeCH$_2$), 31.6 (SeCH$_2$$CH_2$), 65.3 (Se$C$C), 85.7 (SeC$C$); IR (KBr) 2936, 2061, 1637, 1445 cm^{-1}; MS (EI, 70 eV) 496 [M$^+$], 298, 256, 202; HRMS (EI, 70 eV) calcd for $C_{14}H_{12}{}^{80}Se_4$ 499.7600, found 499.7578. Anal. Calcd for $C_{16}H_{16}Se_4$: C, 33.90; H, 2.44. Found: C, 33.91; H, 2.53.

1,6,11,16-Tetraselenacyclooeicosa-2,4,12,14-tetrayne (9(4)) and 1,6,11,16,21,26-Hexaselenacyclotriaconta-2,4,-12,14,22,24-hexayne (10(4)). Starting materials: 2.53 g (13.0 mmol) of **5**, 20.0 mL (30.0 mmol) of MeLi/LiBr in diethyl ether, and 3.90 g (14.0 mmol) of 1,4-diselenocyanatobutane (**7(4)**). Column chromatography afforded 594 mg (16.9%) of **9(4)** and 113 mg (3.2%) of **10(4)** as slightly yellow solids.

9(4): mp 142 °C (explosion); ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 2.05 (m, 8H, SeCH$_2$CH_2), 2.87 (m, 8H, SeCH_2); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 29.4 (CH$_2$), 30.2 (CH$_2$), 64.0 (SeCC), 86.7 (SeCC); IR (KBr) 2926, 2064, 1628, 1438 cm^{-1}; MS (FD+) 526 [M$^+$]. Anal. Calcd for $C_{16}H_{16}Se_4$: C, 36.66; H, 3.08. Found: C, 36.71; H, 3.07.

10(4): mp 90 °C (dec); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.01 (m, 12H, SeCH$_2$CH_2), 2.86 (m, 12H, SeCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.7 (CH$_2$), 29.9 (CH$_2$), 64.4 (SeCC), 86.1 (SeCC); IR (KBr) 2930, 2063, 1628, 1442 cm^{-1}; MS (FD) 786 [M$^+$]. Anal. Calcd for $C_{24}H_{24}Se_6$: C, 36.66; H, 3.08. Found: C, 36.40; H, 3.31.

1,6,12,17-Tetraselenacyclodocosa-2,4,13,15-tetrayne (9(5)) and 1,6,12,17,23,28-Hexaselenacyclotritriaconta-2,4,13,15,24,26-hexayne (10(5)). Starting materials: 2.53 g (13.0 mmol) of **5**, 20.0 mL (30.0 mmol) of MeLi/LiBr in diethyl ether, and 4.06 g (14.5 mmol) of 1,5-diselenocyanatopentane (**7(5)**). Column chromatography afforded 150 mg (4.2%) of **9(5)** and 104 mg (2.9%) of **10(5)** as colorless solids.

9(5): mp 146 °C (dec); ^{1}H NMR (toluene-d_8, 500 MHz) δ 1.09 (quint, ^3J = 7.4 Hz, 4H, SeCH$_2$CH$_2$CH_2), 1.51 (m, 8H, SeCH$_2$CH_2), 2.25 (t, ^3J = 7.4 Hz, 8H, SeCH_2); ^{13}C NMR (toluene-d_8, 125 MHz) δ 29.0 (SeCH$_2$CH$_2$$CH_2$), 29.6 (SeCH$_2$$CH_2$), 30.3 (Se$CH_2$), 64.6 (Se$C$C), 87.8 (SeC$C$); IR (KBr) 2860, 2062, 1628, 1456 cm^{-1}; MS (EI, 70 eV) 554 [M$^+$], 473; HRMS (EI, 70 eV) calcd for $C_{18}H_{20}{}^{78}Se^{80}Se_3$ 553.8234, found 553.8239.

10(5): mp 94 °C; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.51 (quint, ^3J = 6.8 Hz, 6H, SeCH$_2$CH$_2$CH_2), 1.80 (m, 12H, SeCH$_2$CH_2), 2.91 (t, ^3J = 7.1 Hz, 12H, SeCH_2); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 27.9 (SeCH$_2$CH$_2$$CH_2$), 29.2 ($CH_2$), 29.6 ($CH_2$), 66.0 (Se$C$C), 85.6 (SeC$C$); IR (KBr) 2930, 2854, 2061, 1628 cm^{-1}; MS(FD+) 828 [M$^+$].

Preparation of Inclusion Compounds. The polyalkyne cycle was dissolved in the potential guest as the solvent. After the solvent was evaporated at room-temperature, crystals were formed including the desired guest molecule. If the solubility in the desired solvent was insufficient, a small amount of dichloromethane was added.

Preparation of 5-Methoxy-1,6-dithiacyclodeca-4-ene-2-yne (4). To a mixture of 730 mg (10.8 mmol) of copper(I) chloride and 150 mL of concentrated ammonia in 600 mL of methanol dithiadiyne was added **1(4)**. The color changed from blue to green. Then, oygen was bubbled for 2 h through the solution while stirring at room temperature. After aequeous workup and extraction with diethyl ether, 73 mg (9.9%) of **4** was isolated as a colorless solid after column chromatography on silica gel eluting with a mixture of hexane and toluene. After **4**, 60 mg (9.6%) of **2(4)** was isolated.

4: mp 52 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.02 (m, 2H, CH_2), 2.24 (m, 2H, CH_2), 2.90 (m, 2H, SCH_2), 3.13 (m, 2H, SCH_2), 3.66 (s, 3H, CH_3), 5.07 (s, 1H, CH); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.5 (CH$_2$), 29.6 (CH$_2$), 31.3 (CH$_2$), 34.0 (CH$_2$) 58.0 (CH$_3$), 84.8 (CH), 85.8 (CC), 91.3 (CC), 169.2 (CCH); IR (KBr) 3018, 2961, 2146, 1624 cm^{-1}; HRMS (EI, 70 eV) calcd for $C_9H_{12}OS_2$ 200.0330, found 200.0318.

X-ray Diffraction Analyses. The reflections were collected with a CCD diffractometer (Mo Kα radiation, graphite monochromator). Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using SADABS[28] based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods. The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms were calculated according to stereochemical aspects. Structure solution and refinement were carried out with SHELXTL (5.10) software package.[28] ORTEP drawings were obtained using the ORTEP-3 for Windows program by L. Farrugia.[29] CCDC 223391 (**4**), 223392 (**2**(**2**)), 223393 (**2**(**3**)), 223394 (**2**(**4**)), 223395 (**2**(**5**)α), 223396 (**2**(**5**(***β***), 223397 (**9**(**2**)), 223398 (**9**(**3**)), 223399 (**9**(**4**)), 223400 (**9**(**5**)), 223401 (**8**(**3**)), 223402 (**8**(**4**)α), 223403 (**8**(**4**)***β***), 195065 (**8**(**5**)α), 195066 (**8**(**5**)***β***), 223404 (**10**(**4**)α), 223405 (**10**(**4*β***), 195067 (**10**(**5**α), 223406 (**10**(**5**)***β***), 223407 (**10**(**5**)*γ*), 223408 (**10**(**5**)***δ***), 223409 (**10**(**5**)ϵ), 195069 (**10**(**5**)*ζ*), 195068 (**10**(**5*η***), 195072 (**10**(**5**(***θ***), 223410 (**10**(**5*ι***), 195070 (**10**(**5**)*κ*), 223411 (**10**(**5**)*λ*), 223412 (**10**(**5**)***μ***) contain the supplementary crystallographic data for the structures. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk.

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Supporting Information Available: Crystallographic data for all new compounds and inclusion compounds (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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