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A Convenient Approach to 16-, 19-, and 22-Membered 2,2′-Bipyridine Thiacrown Ethers and Their Conformation Preferences

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A convenient, three-step synthesis of 1:1 thiacrown ether macrocycles **5a–c** containing a fused cyclopenteno[*c*]2,2′-bipyridine subunit has been accomplished through first homocoupling of 1,2,4-triazine bisulfides **3a–c** tethered to poly(ethylene glycol) chains with potassium cyanide and second Diels–Alder/retro-Diels–Alder reaction of such obtained thiamacrocycles **4a–c** with 1-pyrrolidino-1-cyclopentene. Macrocycles **5a–c** were oxidized to nonracemic monosulfoxides **6a–c** by using Davis′ oxaziridine and tested in the asymmetric addition of the diethylzinc to benzaldehyde. The crystal structure determinations of **5a–c** and **6b** and theoretical calculations at the DFT/B3LYP/6-311G** level were used to establish their *cis* or *trans* conformations in the solid state and the gas phase.

Introduction

2,2′-Bipyridines (bpy) and their annulated derivatives occupy an important position in many areas of chemistry. They are employed as chelating ligands in the field of catalysis,[1] coordination and supramolecular chemistry,[2] metal-containing polymers,[3] molecular electronics and optoelectronic devices,[4] and as photoactivated species by coordination to transition metals.[5] 2,2′-Bipyridines are also utilized as molecular hosts in bpy-containing macrocycles.[6] Particularly interesting and useful are their annulated derivatives incorporated into the larger macropolycyclic structures, as they form stable luminescent complexes with a variety of lanthanide cations.[7] Attachment of a cycloalkene ring into the bpy core can result in a higher efficiency of metal–ligand interactions as a result of an increase in the basicity of bipyridine nitrogen atoms.[8] Besides the well-known complexation of metal ions,[9] C_2-symmetric 2,2′-bpy crown ethers have been developed recently for the enantiomeric recognition of amino acid derivatives and chiral organic ammonium salts.[10] In view of these results and our continuing interest in bpy-derived cyclophanes,[11] we began exploring the sulfur analogues of such macrocycles in which the sulfur atoms are directly attached to the bpy ring. Such ligands should be able to coordinate to softer metal ions better than those containing nitrogen or oxygen donor atoms. Furthermore, these ligands may constitute a valuable starting material for the synthesis of bpy chiral sulfoxides as catalysts in asymmetric reactions.[12] However, the study of the metal-complexing ability of these interesting compounds has been hampered by the lack of efficient methods for their synthesis.[13] Our ongoing research on ring transformation of biheterocycles revealed that 5,5′-bi-1,2,4-triazines bearing alkylsulfanyl substituents on the triazine rings easily undergo Diels–Alder/retro-Diels–Alder (DA–rDA) reaction with electron-rich dienophiles to give monocyclic or annulated bpy alkyl sulfides in good yields.[14] In this work, we report a new approach to 1:1 thiacrown ether macrocycles and their sulfoxides incorporating a cyclopenteno[*c*]2,2′-bipyridine subunit, as well as X-ray crystallographic analysis of the target ligands. Our preliminary findings[15] and these studies suggest that this approach is fairly general for the preparation of large-sized rings, that is, rings having 13–22 or more atoms.

Results and Discussion

The important features of the synthetic strategy are summarized in Scheme 1, wherein bisulfides **3a–c** tethered to poly(ethylene glycol)chains were envisaged as key intermediates and primary targets of the project. Application of the homocoupling procedure to **3a–c** should provide thiamacrocycles **4a–c**, which may be converted into bipyridine-based thiamacrocycles **5a–c** using DA–rDA reactions. Asymmetric oxidation of the DA–rDA adducts affords the corresponding sulfoxides **6a–c**.

Synthesis of bisulfides **3a–c** requires the use of a tri-, tetra-, and penta(ethylene glycol)dibromides **1a–c**, which can be readily prepared by using literature procedures.[16] Reaction of thiosemicarbazide with 0.5 equiv. of the appropriate poly(ethylene glycol)dibromides **1a–c** in boiling ethanol leads to the corresponding diquaternary salts **2a–c** in excellent yields. The condensation of crude diquaternary

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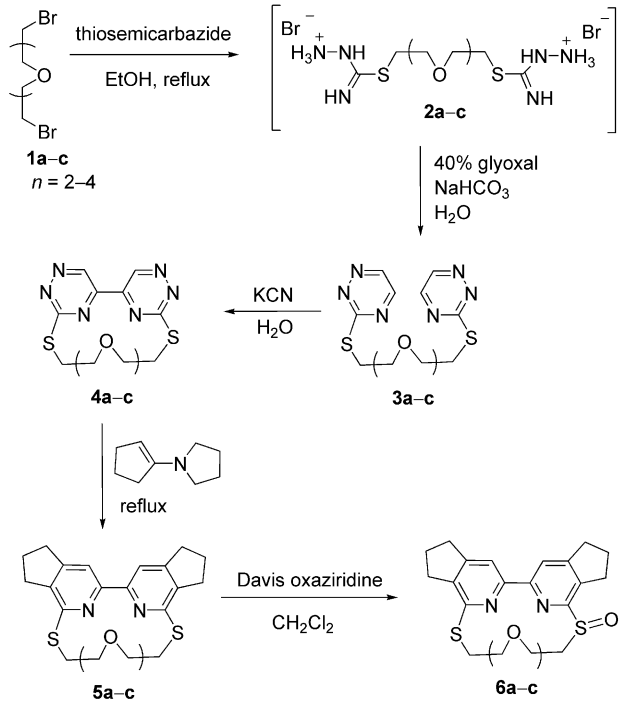


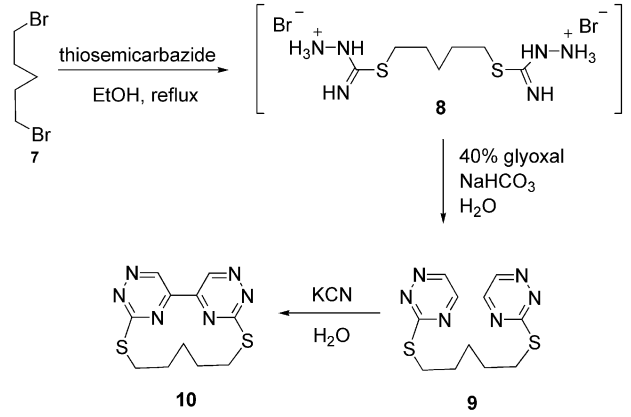
Scheme 1. Synthesis of 1,2,4-triazine bisulfides **3a**–**c**, 5,5′-bi-1,2,4-triazine thiacrown ethers **4a**–**c**, cyclopenteno[*c*]-2,2′-bipyridine-based thiacrown ethers **5a**–**c**, and sulfoxides **6a**–**c**.

salts **2a**–**c** with glyoxal in the presence of sodium hydrogen carbonate affords 1,2,4-triazine bisulfides **3a**–**c** in good yields after flash chromatography (Table 1). The structures of new compounds are clearly supported by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, or HRMS. The ^{1}H NMR spectra exhibited two pairs of doublets between δ = 8.35 and δ = 8.92 ppm corresponding to the protons at C-5 and C-6 of the 1,2,4-triazine unit, in addition to signals ranging from δ = 3.43 to δ = 3.82 ppm for the aliphatic protons of the ethylene glycol units. With bisulfides **3a**–**c** in hand, the next task was to evaluate the homocoupling reaction in the presence of potassium cyanide, leading to macrocycles **4a**–**c**. Previous studies from Paudler et al.[17] showed that treatment of 5-unsubstituted 1,2,4-triazines with potassium cyanide gives predominantly 5,5′-bi-1,2,4-triazine derivatives.

Table 1. Reaction conditions, yields, and melting points of compounds **3a**–**c**, **4a**–**c**, **5a**–**c**, **6a**–**c**, **9**, and **10**.

Compound	Time [h]	Yield [%]	M.p. [°C]
3a	24	64	73–74
3b	24	55	48–49
3c	24	36	49–50
4a	0.25	69	228–229
4b	0.2	70	150–151
4c	0.17	77	108–109
5a	18	68	149–150
5b	14	67	121–122
5c	15	65	167–168
6a	24	41	oil
6b	24	42	163–164
6c	24	51	140–141
9	20	39	35–36
10	24	62	233–234

The possibility of preparing **4a**–**c** by using potassium cyanide for intramolecular dimerization of bisulfides **3a**–**c** was therefore studied. To establish optimal conditions for the dimerization process we first investigated conditions for the homocoupling reaction of 1,5-bis(1,2,4-triazin-3-ylsulfanyl)pentane (**9**) with an excess amount of potassium cyanide in water (Scheme 2). A two-step, one-pot procedure involving *S*-alkylation of thiosemicarbazide with 1,5-dibromopentane (**7**) followed by condensation of the resulting diquaternary salt **8** with glyoxal afforded compound **9**.

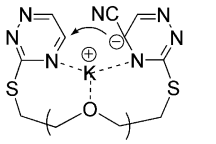


Scheme 2. Synthesis of 1,7-dithia[7]3,3′-5,5′-bis(1,2,4-triazin-3-yl)-cyclophane (**10**).

To avoid unwanted intermolecular side products, the reaction was carried out under high-dilution conditions. After stirring the reaction mixture for 24 h at room temperature, thiacrown ether **10** was obtained in 62% yield, together with some unreacted starting material. In contrast, the reaction between **3a** and potassium cyanide under the same reaction conditions was completed within 15 min (TLC), yielding thiamacrocycle **4a** exclusively. The amount of **4a** formed strongly depended on the reaction time. Increasing the reaction time did not lead to a higher yield of isolated **4a** but instead resulted in partial decomposition of the product. The isolation of compounds **4a**–**c** as the only products in 70–77% yield after reaction of bisulfides **3a**–**c** with potassium cyanide under identical reaction conditions demonstrates the generality of this procedure (see Table 1).

All the reactions were rapid and went to completion within 10–15 min. These results strongly suggest that the template effect of the potassium ion[18] is effective in the case of bisulfides **3a**–**c** tethered to poly(ethylene glycol) chains, and may not be operative for compound **9** without an oxygen atom in the tether. It is reasonable to assume that the reactions of **3a**–**c** proceed by initial addition of the potassium cyanide at position C-5 of the triazine ring in accordance with an intermolecular dimerization process.[17] After adduct formation, preorientation of the corresponding bisulfide takes place as a result of a template reaction that occurs between its coordination sites (oxygen and nitrogen atoms) and the alkaline metal ion. Finally, the template effect involves a cation of structure **3′a**–**c** (Figure 1)

guiding together the 1,2,4-triazine rings, thus increasing the rate of dimerization reaction. It is noteworthy that this mechanism might explain the absence intermolecular dimerization products after treatment of bisulfides **3a**–**c** with potassium cyanide.



3'a–c

Figure 1. The template effect of potassium ion.

The preparation of pyridine or 2,2′-bipyridine derivatives by the inverse-electron-demand DA–rDA reaction of monomeric or dimeric 1,2,4-triazines with enamines is a well-established strategy in organic synthesis.[19] However, the DA–rDA reaction of macrocycles containing the bi-1,2,4-triazine unit has never been studied. It has been previously reported that the DA–rDA reaction of bi-1,2,4-triazines with cyclic enamines without solvent is the method of choice for obtaining cycloalkeno-2,2′-bipyridines.[20] Compound **4a** reacted with 1-pyrrolidino-1-cyclopentene under the same conditions in freshly distilled enamine at 150 °C for 17 h to afford thiacrown ether **5a** in 64% yield. This methodology was shown to be quite general, allowing the preparation of annulated thiamacrocycles **5a**–**c** with an attached cyclopentene ring in good yield (Table 1). The ^{1}H NMR spectroscopic data of thiacrown ethers **5a**–**c** are outlined in the Experimental Section. The preferred conformations of these macrocycles are ascertained by the size of the polythioether bridge and are determined by analyzing the chemical shifts of the bipyridyl hydrogen atoms using literature procedures.[21] The resonances of the bipyridine hydrogen atoms in **5a** and **5b** (δ = 7.36–7.47 ppm) indicate a *cis* arrangement for these macrocycles. In contrast, the chemical shifts of bipyridine protons in **5c** (δ = 7.85 ppm and their downfield shift $\Delta\delta$ = 0.42–0.57 ppm) suggest a *trans* conformation for this pentaethylene chain ligand with the two pyridine nitrogen atoms oriented 180° with respect to each other. This is consistent with the chemical shifts of pyridine protons (δ = 7.85 ppm) in the annulated 6,6′-bis-(methylsulfanyl)-2,2′-bipyridine[20] **11** (see Figure 2) and the crystal structures of compounds **5a**–**c** (see below).

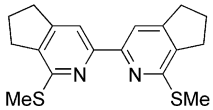


Figure 2. Annulated 6,6′-bis(methylsulfanyl)-2,2′-bipyridine (**11**).

As an extension of these investigations, monosulfoxides **6a**–**c** were obtained after direct asymmetric oxidation in the presence of the chiral oxaziridine developed by Davis et al.[22] The highest enantioselectivity was obtained for sulfoxide **6b**, which contained a 19-membered ring. The preferred conformation of this macrocycle in the solid state was established by X-ray crystal structure analysis. This new class of monosulfoxide ligands **6a**–**c** is currently being tested as a chiral auxiliary in some asymmetric reactions. However, the results obtained in the asymmetric addition of diethylzinc to benzaldehyde demonstrate low catalytic efficiency of the ligands and the *ee* values of the chiral 1-phenyl-1-propanol were much lower than those observed for other catalysts.[23] The application of these chiral sulfoxides as complexing agents is under investigation.

To establish the conformation preferences of annulated 2,2′-bipyridine thiamacrocycles and their ability to complex metal ions, crystal structure analysis of **5a**–**c** and **6b** and theoretical calculations at the DFT/B3LYP/6-311G** level were undertaken. The structures of the molecules are shown in Figure 3. One can see that macrocycles **5a** and **5b** containing 16- and 19-membered rings, respectively, exist in the crystal in the *cis* (*syn*) conformation with a torsion angle N1A–C2A–C2B–N2B about the central bond of the bipyridyl system of –0.6(3)° for **5a** and 0.4(2)° for **5b**. In **5c** with a 22-membered macrocyclic system, the bipyridyl group adopts a *trans* (*anti*) conformation with a torsion angle of 175.21(18)°. In all three molecules, the S10–C11 bonds of the thiaethereal chain are oriented in a *cis* conformation with respect to the N1–C6 bonds of the pyridine rings. The torsion angles N1A–C6A–S10A–C11A and N1B–C6B–S10B–C11B are –6.00(19) and –1.64(18)° in **5a**, –8.5(6) and –1.66(17)° in **5b**, and 23.2(2) and 13.6(2)° in **5c**. A different conformation is observed in **6b**, which was obtained after sulfoxidation of **5b**. The presence of the sulfinyl group causes the pyridine rings to be inclined at an angle of 33.2(1)°. As a result, the bipyridyl group adopts an intermediate conformation in which both pyridine rings are some-

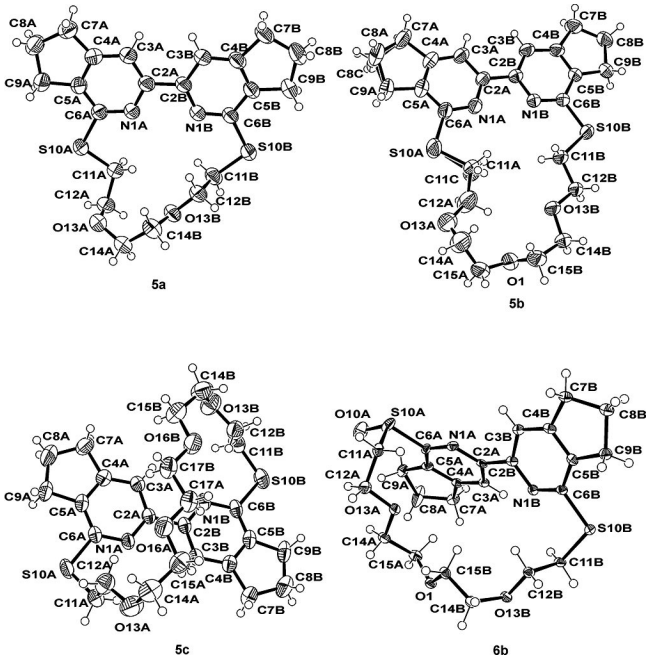


Figure 3. A view of the X-ray molecular structures of **5a**–**c** and **6b** with the atomic labeling scheme. Non-hydrogen atoms are represented by displacement ellipsoids of 50% probability.

where between the perpendicular and parallel positions. The torsion angle N1A–C2A–C2B–N1B is 148.1(3)° in **6b**. The conformation of the thiaethereal chain from the sulfoxide side to the pyridine ring is changed from *cis* to *gauche* with a torsion angle N1A–C6A–S10A–C11A of –63.6(3)°. The torsion angle O10A–S10A–C6A–N1A of –175.9(3)° means that the polarization vectors of the S=O and N–C bonds are in the most profitable antiparallel position and the nonbonding electron pairs of the O and N atoms are located two bonds away from each other. The existence of this electronic effect is confirmed by the charge distribution at the N1A (–0.519 *e*), C6A (+0.158 *e*), S10A (+1.165 *e*), and O10A (–0.967 *e*) atoms, obtained from DFT/B3LYP/6-311G** calculations. These electronic and steric effects of the sulfinyl group and pyridine ring in **6b** probably cause the twisting of the heterorings in the bipyridyl group in the direction of a *trans* conformation, which is not observed in precursor **5b**.

In all molecules investigated, the bond lengths and angles are within normal ranges.[24] They are practically identical within experimental error for the pyridine rings and statistically significant differences appear in the thiaethereal bridges mainly due to large thermal motions. The C_2 symmetry of macrocycles **5a**–**c** is not retained in their crystals because the molecules occupy an asymmetric position in the unit cell. In particular, departure from C_2 symmetry is visible in the symmetry related parts of the thiaethereal bridges in **5a** and **5b**. The torsion angles around following bonds of thiaethereal chains (Table 2) show that the conformations of the symmetry related left (A) and right (B) parts are: *cis-trans-gauche-gauche-gauche-gauche* and *cis-gauche-trans-trans-trans* in **5a**, and *cis-gauche-gauche-gauche-gauche-gauche-gauche* and *cis-trans-trans-trans-trans-gauche-trans* in **5b**. In **5c**, both parts have approximately the same *cis-gauche-trans-trans-gauche-gauche-trans-trans-trans* conformation. The conformations of molecules **5a**–**c** in the

Table 2. Selected torsion angles from X-ray analysis (standard deviations in parentheses) and DFT calculations.

	Torsion angle [°]			Torsion angle [°]	
	X-ray	DFT		X-ray	DFT
5a					
N1A–C2A–C2B–N1B	–0.6(3)	–24.1	N1B–C6B–S10B–C11B	–1.64(18)	11.5
N1A–C6A–S10A–C11A	–6.00(19)	1.4	C6B–S10B–C11B–C12B	–79.71(17)	–84.5
C6A–S10A–C11A–C12A	161.08(16)	154.1	S10B–C11B–C12B–O13B	–176.72(14)	–179.9
S10A–C11A–C12A–O13A	–68.7(2)	–66.0	C11B–C12B–O13B–C14B	–172.36(18)	–176.1
C11A–C12A–O13A–C14A	–101.8(2)	–105.4	C12B–O13B–C14B–C14A	171.80(18)	174.2
C12A–O13A–C14A–C14B	75.4(3)	81.4			
O13A–C14A–C14B–O13B	–76.8(3)	–75.8			
5b					
N1A–C2A–C2B–N1B	0.4(2)	–31.9	N1B–C6B–S10B–C11B	–1.66(17)	7.3
N1A–C6A–S10A–C11A	–8.5(6)	2.5	C6B–S10B–C11B–C12B	174.06(15)	98.6
C6A–S10A–C11A–C12A	–141.7(9)	–148.6	S10B–C11B–C12B–O13B	–179.69(13)	–178.8
S10A–C11A–C12A–O13A	–54.0(12)	–61.8	C11B–C12B–O13B–C14B	–179.68(16)	–165.3
C11A–C12A–O13A–C14A	–93.7(8)	–75.1	C12B–O13B–C14B–C15B	177.50(17)	–171.9
C12A–O13A–C14A–C15A	–71.0(4)	–74.1	O13B–C14B–C15B–O1	67.9(2)	81.7
O13A–C14A–C15A–O1	66.9(4)	78.4	C14B–C15B–O1–C15A	–163.40(16)	–164.5
C14A–C15A–O1–C15B	90.9(3)	94.3			
5c					
N1A–C2A–C2B–N1B	175.21(18)	–162.9	N1B–C6B–S10B–C11B	13.6(2)	13.8
N1A–C6A–S10A–C11A	23.2(2)	15.5	C6B–S10B–C11B–C12B	73.6(2)	77.1
C6A–S10A–C11A–C12A	71.82(19)	77.6	S10B–C11B–C12B–O13B	–171.41(18)	–177.9
S10A–C11A–C12A–O13A	–174.33(19)	–176.8	C11B–C12B–O13B–C14B	172.4(2)	–178.9
C11A–C12A–O13A–C14A	165.8(2)	179.5	C12B–O13B–C14B–C15B	–80.8(3)	–80.6
C12A–O13A–C14A–C15A	–79.6(3)	–81.4	O13B–C14B–C15B–O16B	76.3(3)	76.3
O13A–C14A–C15A–O16A	83.9(3)	76.8	C14B–C15B–O16B–C17B	–176.5(2)	–172.0
C14A–C15A–O16A–C17A	–175.9(2)	–171.7	C15B–O16B–C17B–C17A	175.5(2)	179.6
C15A–O16A–C17A–C17B	176.1(2)	179.8			
O16A–C17A–C17B–O16B	–178.2(2)	–175.4			
6b					
N1A–C2A–C2B–N1B	148.1(3)	144.5	N1B–C6B–S10B–C11B	–15.9(3)	–21.0
N1A–C6A–S10A–C11A	–63.6(3)	–62.9	C6B–S10B–C11B–C12B	–70.7(3)	–71.1
C6A-S10A-C11A-C12A	–69.8(4)	–74.5	S10B–C11B–C12B–O13B	178.8(3)	–178.6
S10A–C11A–C12A–O13A	77.0(4)	82.3	C11B–C12B–O13B–C14B	–168.0(3)	–167.1
C11A–C12A–O13A–C14A	–158.0(4)	–165.2	C12B–O13B–C14B–C15B	85.1(4)	87.1
C12A–O13A–C14A–C15A	172.6(4)	179.5	O13B–C14B–C15B–O1	83.1(4)	83.1
O13A–C14A–C15A–O1	87.3(4)	84.8	C14B–C15B—O1–C15A	–160.9(3)	–152.0
C14A–C15A–O1–C15B	–61.8(5)	–67.1			

crystals are stabilized by the short intramolecular C–H···O and C–H···N contacts listed in Table 3.

Table 3. Short intramolecular interactions (standard deviations in parentheses).

D H A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
5a				
C11–H11D···O13B	0.97	2.47	3.140(3)	126
C11A–H11D···N1A	0.97	2.47	2.862(3)	104
C11B–H11E···N1B	0.97	2.51	2.866(3)	102
5b				
C11A–H11C···N1A	0.97	2.41	2.909(15)	112
C12A–H12C···O1	0.97	2.38	3.130(4)	134
5c				
C11A–H11D···N1A	0.97	2.48	2.853(3)	103
C11B–H11F···N1B	0.97	2.48	2.836(3)	102
C12A–H12C···O16A	0.97	2.47	3.175(4)	130
C12B–H12E···O16B	0.97	2.40	3.084(3)	127

It seems that the ability of the investigated macrocycles to complex metal ions within their internal cavity is strictly dependent on the length of the thiaethereal bridge and the conformation of the bipyridyl group. The X-ray crystallographic data show that the size of the cavity available for complexation increases from 2.448 Å in **5b** to 2.588 Å in **5a** and to 2.611 Å in **6b** but decreases to 2.296 Å in **5c**. This size is calculated as the respective interatomic distance within bipyridine thiacrown ether [N(1B)···H(11D) of 3.618 Å in **5a**, N(1B)···H(11C) of 3.478 Å in **5b**, H(7C)···H-(15F) of 2.996 Å in **5c**, and N(2B)···H(15F) of 3.641 Å in **6b**] minus the sum of the proper atomic radii (0.68 and 0.35 Å for the N and H atom, respectively[25]). The smaller size of the cavity in **5b** in comparison to that in **5a** is related to the geometry perturbation within the thiaethereal bridge due to the positional disorder of the C-11 atom. Theoretical calculations at the DFT/B3LYP/6-311G** level showed that the conformations obtained after energy minimization and geometry optimization (Figure 4) gave somewhat larger size of cavities. They are 2.554, 2.451, 2.776, and 2.770 Å in **5a**, **5b**, **5c**,– and **6b**, respectively. The sizes of the internal cavities obtained from theoretical calculations are larger in comparison to those observed in crystal structures. This may be attributed to a change in the calculated N1A–C2A–C2B–N1B torsion angles to –24.1, –31.9, –162.9, and 144.5° for **5a**, **5b**, **5c**, and **6b**, respectively. Theoretical calculations were performed in the gas phase and gave the conformations of the isolated molecules, whereas the mutual, nearly parallel orientation of the pyridine rings observed in the crystal structures of **5a** and **5b** may be constrained by π···π interactions observed in their crystals. The pyridine rings (A) of compound **5a** overlap each other with a π···π distance of 3.556 Å. Similarly, overlapping of inversion-related pyridine rings (B) with a π···π distance of 3.573 Å is observed in the crystal structure of **5b**. The small changes in the other calculated torsion angles across the bonds of thiaethereal chain (Table 2) do not have a significant influence on the cavity diameter. One can conclude that the *cis* conformation of the bipyridyl group of the macrocycle favors complexation within its cavity, whereas the *trans* conformation prefers external complexation with the central ethereal bridging oxygen atoms. The natural bond order (NBO) charges calculated at the DFT/B3LYP/6-311G** level on the nitrogen atoms are –0.496 and –0.493 *e* for **5a**, –0.495 and –0.492 *e* for **5b**, –0.552 and –0.552 *e* for **5c**, and –0.519 and –0.527 *e* for **6b**. The NBO charges on the oxygen atoms are –0.604 and –0.620 *e* (O13) for **5a**, –0.608 and –0.605 *e* (O13) and –0.616 *e* (O1) for **5b**, –0.608 and –0.608 *e* (O13) and –0.511 and –0.511 *e* (O16) for **5c**, and –0.616 and –0.603 *e* (O13) and –0.603 *e* (O1) for **6c**. These NBO values do not depend on the length of the thiaethereal bridge and are favorable for the complexation of metal ions.

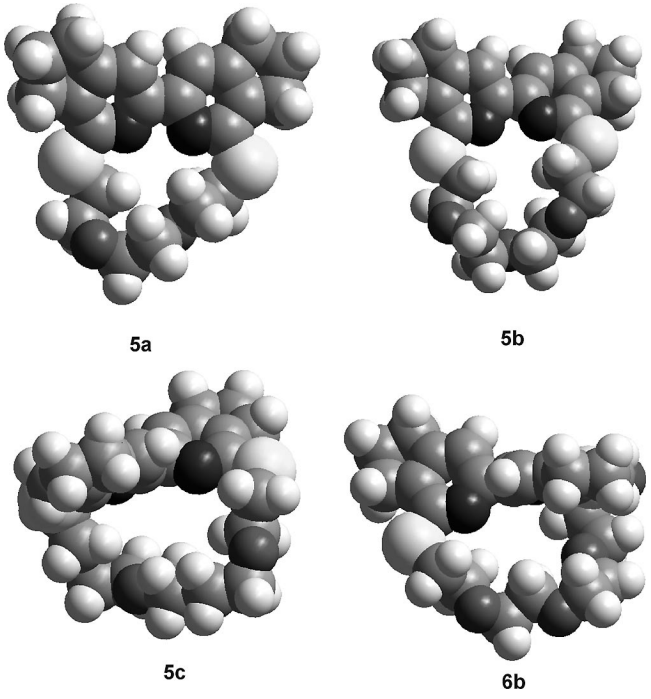


Figure 4. B3LYP/6-311G** DFT calculations molecular structures of **5a**–**c** and **6b** in the model of overlapping spheres.

Conclusions

The synthetic protocol described herein provides expedient access to a novel family of 1:1 thiacrown ether macrocycles containing an annulated 2,2′-bipyridine subunit from commercially available reagents. The method is fairly general and the yields of each of the three consecutive steps required are either acceptable or very good. This fact facilitates further study of the metal-complexing ability of the macrocycles as well as their use as starting materials in the synthesis of chiral sulfoxides for asymmetric catalysis. The preferred conformations of these macrocycles are ascertained by the size of the polyether bridge and can be determined by NMR spectroscopy and X-ray crystal structure analysis. Their abilities to complex metal ions are confirmed by using theoretical calculations at the DFT/B3LYP/6-311G** level.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were determined at 200 and 50 MHz, respectively, with a Varian Gemini spectrometer. Chemical shifts (δ) are given in parts per million and coupling constants are given as absolute values expressed in Hertz. Mass spectra were obtained by using AMD 604 (AMD Intectra GmbH, Germany) and GC–MS QP 5050 Shimadzu (30 m × 0.25 mm ID-BPX 5 0.25 mm) spectrometers. Elemental analyses were recorded with a Perkin–Elmer 2400-CHN analyzer, and the results for indicated elements were within 0.3% of the calculated values. Optical rotation values were measured at room temperature with a JASCO P-2000 polarimeter. The *ee* values were determined by HPLC analysis by using a chiral stationary phase column (chirobiotic T). Thin layer chromatography (TLC) was carried out on aluminum sheets precoated with silica gel 60 F_{254} (Merck). Column chromatography separations were performed by using Merck Kieselgel 60 (0.040–0.060 mm). Solvents were dried and distilled according to standard procedures. All reagents were purchased from Aldrich.

General Procedure for the Preparation of 1,2,4-Triazine Sulfides 3a–c and 9: A solution of thiosemicarbazide (14.28 mmol) and the corresponding dibromides **1a**–**c** and **7** (7.28 mmol) in absolute ethanol (40 mL) was stirred at reflux until TLC analysis indicated that the thiosemicarbazide was consumed. Ethanol was then evaporated, and a solution of glyoxal (40% solution in water, 2.1 mL, 14.28 mmol) and sodium hydrogen carbonate (1.2 g, 14.28 mmol) in ice water (40 mL) was added to the brown residue containing hydrobromic salt **2a**–**c** or **8**. After stirring at room temperature for 30 min, methanol (55 mL) was added, and the mixture was stirred at room temperature for 24 h. Methanol was evaporated in vacuo and the aqueous layer was extracted with CH_2Cl_2 (5 × 10 mL). After evaporation of the solvent from the combined extracts, the remaining residue was purified by column chromatography (CH_2Cl_2/acetone, 10:1).

1,8-Bis(1,2,4-triazin-3-ylsulfanyl)-3,6-dioxaoctane (3a): Spectral data is described in a previous communication.[15]

1,11-Bis(1,2,4-trizin-3-ylsulfanyl)-3,6,9-trioxaundecane (3b): Yield: 3.0 g, 55%. M.p. 48–49 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.48 (t, J = 6.4 Hz, 4 H, CH_2), 3.67 (s, 8 H, CH_2), 3.82 (t, J = 6.4 Hz, 4 H, CH_2), 8.36 (d, J = 2.4 Hz, 2 H, triazine hydrogen), 8.92 (d, J = 2.4 Hz, 2 H, triazine hydrogen) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.1 (SCH_2), 69.2 (OCH_2), 70.3 (OCH_2), 70.4 (OCH_2), 145.3, 148.1, 173.8 (triazine carbon atoms) ppm. HRMS (EI): calcd. for $C_{14}H_{20}N_6O_3S_2$ 384.10383; found 384.10485.

1,14-Bis(1,2,4-trizin-3-ylsulfanyl)-3,6,9,12-tetrakisoxatetradecane (3c): Yield: 2.19 g, 36%. M.p. 49–50 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.43 (t, J = 6.6 Hz, 4 H, CH_2), 3.62 (s, 12 H, CH_2), 3.77 (t, J = 6.6 Hz, 4 H, CH_2), 8.35 (d, J = 2.4 Hz, 2 H, triazine hydrogen), 8.91 (d, J = 2.4 Hz, 2 H, triazine hydrogen) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.1 (SCH_2), 69.2 (OCH_2), 70.3 (OCH_2), 70.4 (OCH_2), 70.5 (OCH_2), 145.3, 148.1, 173.8 (triazine carbon atoms) ppm. HRMS (EI): calcd. for $C_{16}H_{24}N_6O_4S_2$ 428.13005; found 428.13154.

1,5-Bis(1,2,4-trizin-3-ylsulfanyl)-pentane (9): Yield: 1.63 g, 39%. M.p. 35–36 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.58–1.72 (m, 2 H, CH_2), 1.75–1.86 (m, 4 H, CH_2), 3.24 (t, J = 7.3 Hz, 4 H, CH_2), 8.35 (d, J = 2.4 Hz, 2 H, triazine hydrogen), 8.91 (d, J = 2.4 Hz, 2 H, triazine hydrogen) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.7 (CH_2), 28.2 (CH_2), 30.1 (SCH_2), 145.1, 148.0, 174.0 (triazine carbon atoms) ppm. HRMS (EI): calcd. for $C_{11}H_{14}N_6S_2$ 294.07214; found 294.07134.

General Procedure for the Preparation of 5,5′-Bi-1,2,4-triazine-Containing Thiamacrocycles 4a–c and 10: A suspension of compound **3a**–**c** or **9** (0.59 mmol) in water (134 mL) was stirred at 40 °C until complete dissolution. After cooling to room temperature, potassium cyanide (0.137 g, 2.12 mmol) was added as a solid, and the resulting mixture was stirred for the period of time indicated in Table 1. The mixture was extracted with CH_2Cl_2 (5 × 50 mL). The combined extracts were dried with $MgSO_4$, filtered, and concentrated in vacuo. The crude products were purified by column chromatography (CH_2Cl_2/acetone, 10:1) to give pure compounds **4a**–**c** and **10**.

4,7-Dioxa-1,10-dithia[10]3,3′-5,5′-bis(1,2,4-triazin-3-yl)cyclophane (4a): Spectral data and microanalysis are described in a previous communication.[15]

4,7,10-Trioxa-1,13-dithia[13]3,3′-5,5′-bis(1,2,4-triazin-3-yl)cyclophane (4b): Yield: 0.16 g, 70%. M.p. 150–151 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.25–3.27 (m, 4 H, CH_2), 3.44–3.46 (m, 4 H, CH_2), 3.54 (t, J = 5.8 Hz, 4 H, CH_2), 3.81 (t, J = 5.8 Hz, 4 H, CH_2), 9.67 (s, 2 H, triazine hydrogen) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.2 (SCH_2), 69.9 (OCH_2), 71.0 (OCH_2), 71.5 (OCH_2), 142.1, 150.0, 174.6 (triazine carbon atoms) ppm. $C_{14}H_{18}N_6O_3S_2$ (382.46): calcd. C 43.98, H 4.71, N 21.99; found C 44.01, H 4.80, N 21.75.

4,7,10,13-Tetraoxa-1,16-dithia[16]3,3′-5,5′-bis(1,2,4-triazin-3-yl)-cyclophane (4c): Yield: 0.19 g, 77%. M.p. 108–109 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.11 (s, 4 H), 3.36–3.40 (m, 4 H, CH_2), 3.54–3.62 (m, 8 H, CH_2), 3.85 (t, J = 6.0 Hz, 4 H, CH_2), 9.88 (s, 2 H, triazine hydrogen) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.1 (SCH_2), 70.1 (OCH_2), 70.3 (OCH_2), 70.4 (OCH_2), 70.9 (OCH_2) 142.1, 149.7, 174.1 (triazine carbon atoms) ppm. HRMS (EI): calcd. for $C_{16}H_{22}N_6O_4S_2$ 426.11440; found 426.11344.

1,7-Dithia[7]3,3′-5,5′-bis(1,2,4-triazin-3-yl)cyclophane (10): Yield: 0.11 g, 62%. M.p. 233–234 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.54–1.66 (m, 2 H, CH_2), 1.97–2.11 (m, 4 H, CH_2), 3.06–3.14 (m, 4 H, CH_2), 9.50 (s, 2 H, triazine hydrogen) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.9 (CH_2), 28.4 (CH_2), 31.8 (SCH_2), 140.9, 145.2, 148.1 (triazine carbon atoms) ppm. HRMS (EI): calcd. for $C_{11}H_{12}N_6S_2$ 292.05649; found 292.05728.

General Procedure for the Preparation of Thiacrown Ethers 5a–c: Compounds **4a**–**c** (2.96 mmol) were added to freshly distilled 1-pyrrolidine-1-cyclopentene (2.43 g, 17.75 mmol). The mixture was heated at 150 °C for 18 h and then concentrated in vacuo. The residue was purified by column chromatography (CH_2Cl_2/acetone, 50:1) to give pure compounds **5a**–**c**.

4,7-Dioxa-1,10-dithia[10](6,6′)-2,2′-bis(cyclopenta[*c*]pyridin-2-yl)-cyclophane (5a): Spectral data and microanalysis are described in a previous communication.[15]

4,7,10-Trioxa-1,13-dithia[13](6,6′)-2,2′-bis(cyclopenta[*c*]pyridin-2-yl)cyclophane (5b): Yield: 0.91 g, 67%. M.p. 121–122 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.14 (q, J = 7.4 Hz, 4 H, CH_2), 2.85 (t, J = 7.4 Hz, 4 H, CH_2), 2.95 (t, J = 7.6 Hz, 4 H, CH_2), 3.40–3.45 (m, 4 H, CH_2), 3.52–3.65 (m, 8 H, CH_2), 3.78–3.85 (m, 4 H, CH_2), 7.47 (s, 2 H, pyridine hydrogen) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.2, 28.7, 30.1, (cyclopentane carbon atoms), 32.9 (SCH_2), 69.6 (OCH_2), 70.6 (OCH_2), 71.2 (OCH_2), 114.3, 137.1, 152.9, 153.5, 155.1 (pyridine carbon atoms) ppm. HRMS (EI): calcd. for $C_{24}H_{30}N_2S_2O_3$ 458.16979; found 458.16879.

4,7,10,13-Tetraoxa-1,16-dithia[16](6,6′)-2,2′-bis(cyclopenta[*c*]pyridine-2-yl)cyclophane (5c): Yield: 0.96 g, 65%. M.p. 167–168 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.14 (q, J = 7.4 Hz, 4 H, CH_2), 2.85

(t, J = 7.4 Hz, 4 H, CH_2), 2.97 (t, J = 7.4 Hz, 4 H, CH_2), 3.10 (s, 4 H, CH_2), 3.34–3.39 (m, 4 H, CH_2), 3.55–3.62 (m, 8 H, CH_2), 3.76–3.82 (m, 4 H, CH_2), 7.89 (s, 2 H, pyridine hydrogen) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.2, 28.6, 30.1 (cyclopentane carbon atoms), 33.1 (SCH_2), 69.8 (OCH_2), 70.2 (OCH_2), 70.4 (OCH_2), 71.2 (OCH_2), 113.7, 137.4, 152.1, 153.7, 154.3 (pyridine carbon atoms) ppm. HRMS (EI): calcd. for $C_{26}H_{34}N_2S_2O_4$ 502.19600; found 502.19555.

General Procedure for the Preparation of Sulfoxides 6a–c (Davis Method): To a solution of sulfide **5a**–**c** (1 mmol) in anhydrous dichloromethane (30 mL) was added (+)-(8,8′-dichlorocamphoryl-sulfonyl)oxaziridine (0.75 mmol), and the reaction mixture was stirred at room temperature for 24 h. The solvent was evaporated, and the residue was purified by flash chromatography (CH_2Cl_2/acetone, 10:1.5) to yield pure monosulfoxide **6a**–**c**.

4,7-Dioxa-1,10-dithia[10](6,6′)-2,2′-bis(cyclopenta[*c*]pyridin-2-yl)cyclophane Sulfoxide (6a): Yield: 0.17 g, 41% (27%*ee*), oil. $[a]_D^{20}$ = +23 (c = 1.0, CH_2Cl_2). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.12–2.26 (m, 4 H), 2.78–2.86 (m, 2 H), 2.93–3.00 (m, 4 H), 3.27–4.08 (m, 13 H), 4.13–4.23 (m, 1 H), 7.38 (s, 1 H), 7.64 (s, 1 H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 24.2, 25.2, 27.3, 29.1, 29.9, 32.0 (cyclopentane carbon atoms), 32.9 (SCH_2), 55.3 ($SOCH_2$), 64.7 (OCH_2), 70.3 (OCH_2), 70.8 (OCH_2), 70.9 (OCH_2), 114.4, 118.9, 137.1, 139.2, 153.4, 153.9, 155.1, 158.1, 158.6 (pyridine carbon atoms) ppm. HRMS (EI): calcd. for $C_{22}H_{26}N_2S_2O_3$ 430.13848; found 430.13906.

4,7,10-Trioxa-1,13-dithia[13](6,6′)-2,2′-bis(cyclopenta[*c*]pyridin-2-yl)cyclophane Sulfoxide (6b): Yield: 0.20 g, 42% (46%*ee*). M.p. 163–164 °C. $[a]_D^{20}$ = –97 (c = 1.0, CH_2Cl_2). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.00–2.11 (m, 4 H), 2.75–2.83 (m, 2 H), 2.85–3.13 (m, 4 H), 3.19–3.81 (m, 18 H), 4.05–4.17 (m, 1 H), 7.78 (s, 1 H), 8.80 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.1, 25.2, 27.5, 29.1, 29.9, 32.0 (cyclopentane carbon atoms), 32.8 (SCH_2), 52.1 ($SOCH_2$), 61.8, 68.9, 69.4, 70.0, 70.6, 70.7 (OCH_2), 114.1, 118.7, 137.7, 139.4, 151.9, 153.5, 154.1, 154.9, 156.2, 157.5 (pyridine carbon atoms) ppm. HRMS (EI): calcd. for $C_{24}H_{30}N_2S_2O_4$ 474.16470; found 474.16528.

4,7,10,13-Tetraoxa-1,16-dithia[16](6,6′)-2,2′-bis(cyclopenta[*c*]-pyridin-2-yl)cyclophane Sulfoxide (6c): Yield: 0.26 g, 51% (27%*ee*). M.p. 140–141 °C. $[a]_D^{20}$ = –34 (c = 1.6, CH_2Cl_2). ^1H NMR (200 MHz, $CDCl_3$): δ = 2.07–2.24 (m, 4 H), 2.79–2.92 (m, 2 H), 2.94–3.04 (m, 4 H), 3.12–3.80 (m, 21 H), 4.05–4.16 (m, 1 H), 7.99 (s, 1 H), 8.29 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.2, 25.2, 28.2, 29.2, 30.0, 32.2 (cyclopentane carbon atoms), 32.9 (SCH_2), 51.4 ($SOCH_2$), 62.0 (OCH_2), 70.4–71.0 (OCH_2, 7 C overlapped), 113.8, 118.1, 137.9, 139.8, 152.2, 153.0, 154.2, 154.5, 156.3, 157.7 (pyridine carbon atoms) ppm. HRMS (EI): calcd. for $C_{26}H_{34}N_2S_2O_5$ 518.19091; found 518.19026.

X-ray Structure Determinations: X-ray data of **5a** were collected with a Kuma KM4 diffractometer; crystal sizes 0.20 × 0.20 × 0.10 mm, Cu-K_α (λ = 1.54178 Å) radiation, $\omega/2\theta$ scans. Data collections for **5b**, **5c**, and **6b** were performed with a Bruker SMART APEX II CCD diffractometer; crystal sizes 0.50 × 0.24 × 0.03 mm (**5b**), 0.42 × 0.22 × 0.14 mm (**5c**), and 0.35 × 0.14 × 0.07 mm (**6b**), Mo-K_α (λ = 0.71073 Å) radiation, ω scans. All structures were solved by direct methods by using SIR92[26] and refined by full-matrix least-squares with SHELXL97.[27] The H atoms were positioned geometrically and treated as riding on their parent C atoms with C–H distances of 0.93 Å (aromatic) and 0.97 Å (CH_2). All H atoms were refined with isotropic displacement parameters taken as 1.5 times those of the respective parent atoms. All calculations were performed using WINGX version 1.64.05 package.[28] CCDC-773916 (for **5a**), -773917 (for **5b**), -773918 (for **5c**), and -773919 (for **6b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 5a: $C_{22}H_{26}N_2O_2S_2$, M = 414.57, monoclinic, space group $C2/c$, a = 32.897(3) Å, b = 13.699(1) Å, c = 9.263(1) Å, β = 103.99(1)°, V = 4050.6(7) Å^3, Z = 8, $d_{calcd.}$ = 1.360 Mg m^{-3}, F(000) = 1760, μ(Cu-K_α) = 2.546 mm^{-1}, T = 293 K, 5004 measured reflections (θ range 2.77–l80.24°), 4401 unique reflections (R_{int} = 0.027), final R = 0.044, wR = 0.123, S = 1.033 for 3372 reflections with $I > 2\sigma(I)$.

Crystal Data for 5b: $C_{24}H_{30}N_2O_3S_2$, M = 458.62, triclinic, space group $P\bar{1}$, a = 7.4649(3) Å, b = 8.8778(3) Å, c = 18.2591(7) Å, α = 96.955(1)°, β = 91.416(1)°, γ = 107.796(1)°, V = 1141.24(7) Å^3, Z = 2, $d_{calcd.}$ = 1.335 Mg m^{-3}, F(000) = 488, μ(Mo-K_α) = 0.262 mm^{-1}, T = 293 K, 30461 measured reflections (θ range 1.13–31.26°), 7420 unique reflections (R_{int} = 0.019), final R = 0.055, wR = 0.167, S = 1.049 for 5152 reflections with $I > 2\sigma(I)$. The final residual electron-density maps showed that the C8A and C11A atoms are disordered over two sites. The occupancy factors (s.o.f.) for the split carbon atoms were refined to 0.63 and 0.37.

Crystal Data for 5c: $C_{26}H_{34}N_2O_4S_2$, M = 502.67, triclinic, space group $P\bar{1}$, a = 8.607(3) Å, b = 12.140(3) Å, c = 12.276(3) Å, α = 91.62(1)°, β = 94.93(1)°, γ = 91.59(1)°, V = 1276.9(6) Å^3, Z = 2, $d_{calcd.}$ = 1.307 Mg m^{-3}, F(000) = 536, μ(Mo-K_α) = 0.243 mm^{-1}, T = 293 K, 29694 measured reflections (θ range 1.67–25.78°), 4893 unique reflections (R_{int} = 0.035), final R = 0.056, wR = 0.149, S = 1.052 for 3733 reflections with $I > 2\sigma(I)$.

Crystal Data for 6b: $C_{24}H_{30}N_2O_4S_2$, M = 474.62, monoclinic, space group $C2/c$, a = 26.888(2) Å, b = 13.060(1) Å, c = 14.951(1) Å, β = 120.58(1)°, V = 4520.0(6) Å^3, Z = 8, $d_{calcd.}$ = 1.395 Mg m^{-3}, F(000) = 2016, μ(Mo-K_α) = 0.270 mm^{-1}, T = 90 K, 37032 measured reflections (θ range 1.76–25.52°), 4182 unique reflections (R_{int} = 0.121), final R = 0.080, wR = 0.156, S = 1.294 for 3816 reflections with $I > 2\sigma(I)$.

Theoretical Calculations: Calculations at the DFT/B3LYP level with 6-311G** basis set implemented in GAUSSIAN 03[29] were carried out by using natural bond order (NBO) analysis to investigate the conformational preferences of **5a**–**c** and **6b**. The structures were fully optimized without any symmetry constraint and the initial geometries were built from the crystallographic data of **5a**–**c** and **6b**.

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