Benzoyl-Substituted Tetrathia[1.1.1.1]metacyclophanes: High-Yield Synthesis, Crystal Structure, and Redox Properties

Torsten Freund, Christian Kübel, Martin Baumgarten, Volker Enkelmann, Liletta Gherghel, Ronald Reuter, and Klaus Müllen*

Max-Planck-Institute for Polymer Research,
Ackermannweg 10, D-55128 Mainz, Germany

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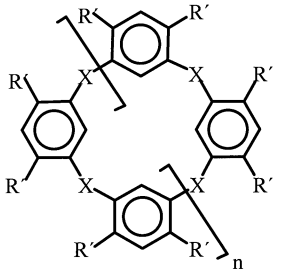
We report a high-yield synthesis of 3,5,17,19-tetrakis(4′-alkylbenzoyl)-1,8,15,22-tetrathia[1.1.1.1]metacyclophanes **7**[1] via condensation of dithioresorcinols **3** with benzoyl substituted *meta*-dichlorobenzenes **6**. The underlying reaction mechanism is discussed. The solid-state structure of the macrocycle and the reduction properties of **7** have also been investigated.

Introduction

Macrocyclic building blocks have attracted considerable interest in supramolecular chemistry[2]. Much work has been devoted to calixarenes **1a**[3][4] and some of their heteroanalogues **1b**−**d**[5] because of their specific host-guest interactions with organic molecules or metal ions. These investigations provide evidence that the incorporation of heteroatoms into the macrocyclic unit enhances the binding of a guest molecule or an ion.



a: X = CHR′′, CH
b: X = S
c: X = O
d: X = SiR′′

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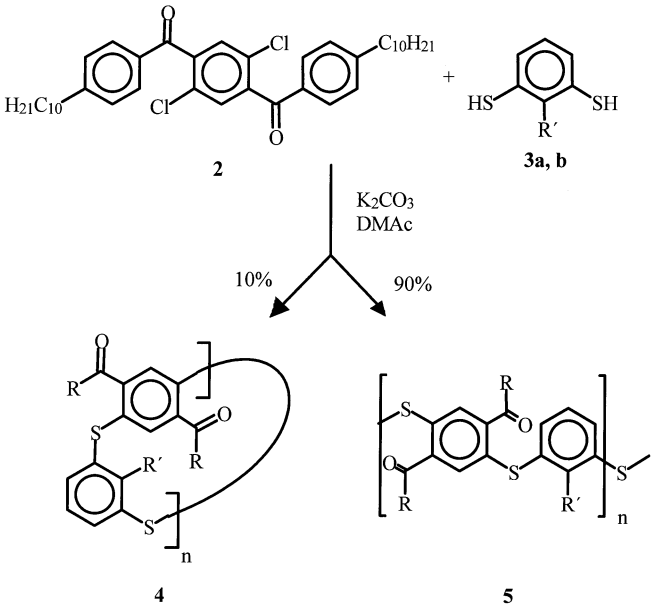
As part of our research on poly(*para-meta*-phenylene sulfide)s **5**[6] we have found an efficient route to the related macrocyclic compounds **7a-g**. As in the polymer case, the cyclophanes carry long *n*-alkyl substituents in order to enhance the solubility in common organic solvents. The benzoyl substituents of the aromatic dichlorides **6a-f** provide the necessary activation to allow the synthesis of the tetrathia[1.1.1.1]metacyclophanes **7** via a nucleophilic aromatic substitution reaction. The astonishingly efficient formation of **7**, and moreover, its dynamic properties, solid state structure and reduction behavior will be the topic of this paper.

Results and Discussion

Syntheses and Characterization of Products: Aromatic dichlorides **2** and aromatic dithiols **3** are useful monomers in the synthesis of substituted high molecular weight poly(*para-meta*-phenylene sulfide)s **5** via nucleophilic substitution, if the aromatic chlorides are activated by electron withdrawing groups, such as benzoyl substituents[6]. If 1,4-bis-(4′-*n*-alkyl-benzoyl)-2,5-dichlorobenzenes **2** are treated with dithioresorcinol (**3a**) or 2-methyldithioresorcinol (**3b**), linear polymers **5** are the major products, whereas the formation of cyclic phenylene sulfide oligomers **4** is observed only in 10% yield (Scheme 1)[6]. Surprisingly, the isomeric 1,3-bis(4′-*n*-alkylbenzoyl)-4,6-dichlorobenzenes **6** yielded a different product distribution if they were subjected to condensation with dithioresorcinols **3a** or **3b** (Scheme 2).

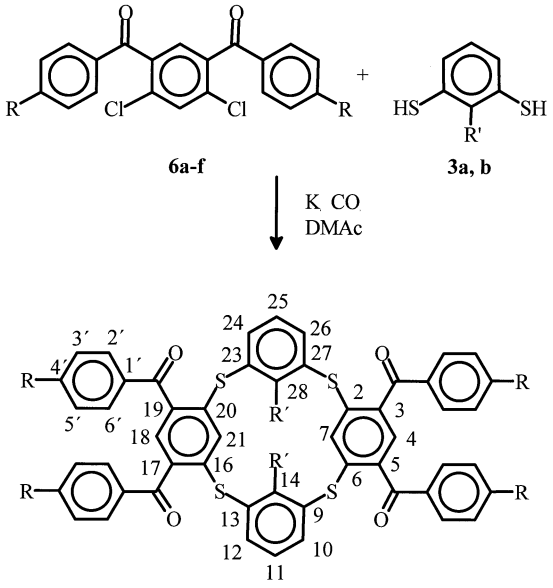
Scheme 1. Synthesis of *para-meta*-bonded phenylene sulfides (R = Ph-*n*-$C_{10}H_{21}$, a: R′ = H, b: R′ = CH_3)



In a typical procedure, a stoichiometric amount of potassium carbonate was added to a 0.1 M suspension of the monomers in *N,N*-dimethylacetamide (DMAc) under an argon atmosphere. The reaction mixture was heated to 80−100 °C for 6 to 12 h before the raw product was precipitated into the twofold volume of 10% acetic acid. Gel per-

  1434−193X/98/0404−0555 $ 17.50+.50/0

Scheme 2. Synthesis of 3,5,17,19-tetrakis(4′-alkylbenzoyl)-1,8, 15,22-tetrathia[1.1.1.1]metacyclophanes **7**

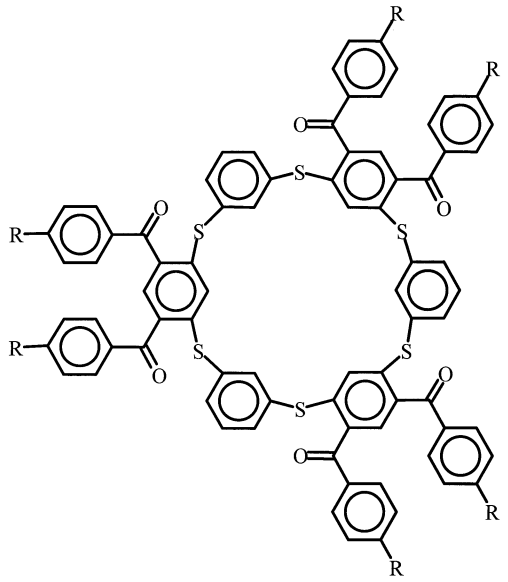


6a-f **3a, b**

7a-g

a: R′ = H, R = H; **b**: R′ = H, R= *t*-Bu; **c**: R′ = H, R = *n*-C_6H_{13}; **d**: R′ = H, R = *n*-$C_{10}H_{21}$; **e**: R′ = H, R = *n*-$C_{12}H_{25}$; **f**: R′ = H, R = *n*-$_{16}H_{33}$; **g**: R′ = CH_3, R = *n*-$C_{10}H_{21}$.

meation chromatographic (GPC) analysis of the raw product revealed the formation of two low molecular-weight species in the ratio 20:1. The major component was identified as **7** by field desorption (FD) mass spectrometry, whereas the minor one was its higher homologue **8** containing six *meta*-phenylene sulfide subunits.



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In order to purify **7** on a preparative scale the raw material was reprecipitated from dichloromethane solution with *n*-hexane, followed by column chromatography on silica gel with a mixture of petroleum ether/dichloromethane (4:1). Thereby **7** was obtained in high yields, for example **7b** was obtained in 90% yield.

Further experiments revealed a remarkable reactivity of the carbon-sulfur bonds. When **7** was treated with a fourfold excess of thiophenolate under the same conditions as used for the formation of **7**, the decomposition products **9**−**13** (Scheme 3) were observed in the FD-mass spectrometric analysis. The reaction of **7** with a large excess of thiophenolate even led to a complete reaction and the diketone **13** was the only product obtained.

We attempted to synthesize the linear poly(*meta*-phenylene sulfide) **14** by ring opening polymerization of **7** using a small amount of potassium thiophenolate to initiate the reaction; however, instead of any high molecular weight products, the starting material was recovered accompanied by trace amounts of **9**. Since these results indicate the reversibility of the carbon-sulfur bond formation, the macrocycle **7** has to be the thermodynamically favored product among all conceivable reaction products.

Recently the use of template effects has been reported to increase the efficiency in calixarene synthesis[7] compared to standard methods[8]. We therefore suspected a similar mechanism to be the reason for the formation of the macrocycle **7**, but not the linear polymer **14**. This hypothesis was examined through condensation of **3** and **6**, conducted in the presence of different bases. The use of sodium and barium carbonate resulted only in slightly lower yields of the macrocycle, but complexation of potassium counter ions by 18-crown[6]ether led to the formation of the poly(*m*-phenylene sulfide) **14** as the main product[9]. On the other hand, potassium carbonate itself produced excellent yields for **7**. Moreover, this procedure no longer necessitates the inconvenient high-dilution conditions generally applied for cyclophane syntheses[8].

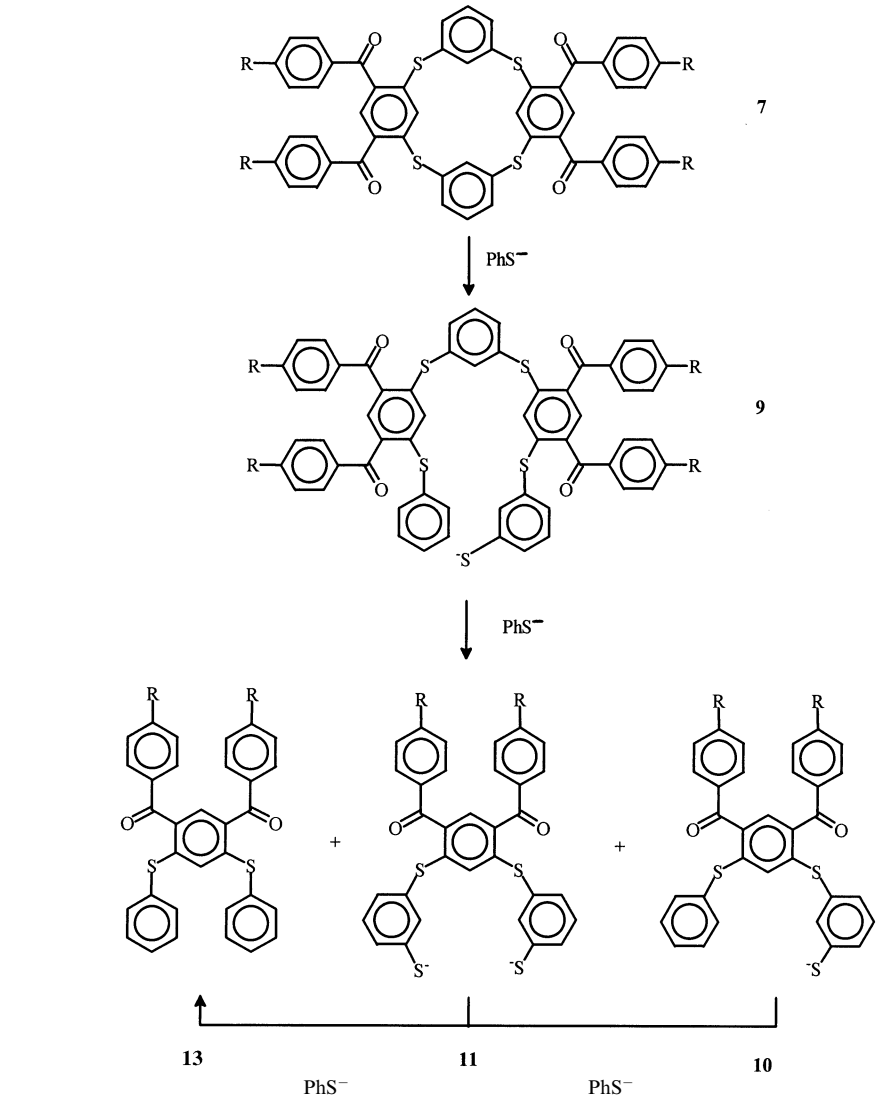
The remarkable difference to the synthesis of poly(phenylene sulfide)s (PPS)[10] from aromatic dibromides and aromatic dithiols must be due to a completely different reaction mechanism: while the standard preparation of PPS by Hill et al.[10] proceeds through a well established radical chain mechanism[11], the above results obtained for the formation of **7** point towards an *ipso*-Meisenheimer complex as an intermediate.

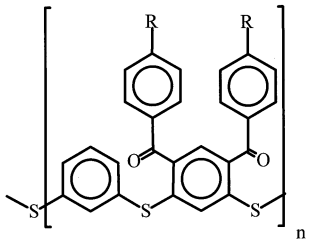
^{1}H-NMR spectroscopic analysis supports the proposed structure of **7**. The aromatic AA′BB′ system (H-2′, 6′ and H-3′, 5′) gives rise to two doublets and the AB_2-spin system (H-11, 25 and H-10, 12, 24, 26) appears as a triplet and a doublet. The remaining three singlets are assigned to H-7, 21, H-4, 18 and to H-14, 28. The singlet due to H-14, 28 is broadened by an unresolved ^4J-coupling.

The ^{13}C-NMR resonances of **7** can be readily assigned by comparison with the model compounds **13** and **15** and by using a *J*-modulated spin-echo experiment (see Experimental Section).

The hydrogen atoms H-7, 21 and H-14, 28 in compound **7** are pointing inside the macrocycle. Their ^{1}H-NMR signals are shifted to low field by Δ 0.25 as compared to the corresponding protons in the model compounds **13** and **15**. The connectivity of C-7, 21 in the macrocycle **7** and C-2 in

Scheme 3. Transformation of tetrathia[1.1.1.1]metacyclophane **7** upon reaction with thiophenolate; R = n-$C_{10}H_{21}$





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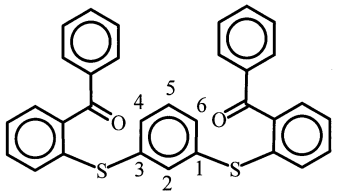

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model compounds **13** and **15** is the same. The deshielding observed for H-7, 21 and H-14, 28 is therefore attributed to the influence of the diamagnetic ring current[12] of the aromatic groups. Thus, the time averaged conformation of the macrocycle **7** at room temperature is a more or less planar one. This conformation with C_{2V}-symmetry as detected by the NMR measurements at room temperature originates from a rapid flipping process of the phenylene rings of the macrocyclic unit. From room temperature to 213 K, the NMR spectra of **7b** in [D_8]THF show nearly no change in line shape and only a small shift of the resonance frequencies of the benzoyl protons. Below 213 K, the NMR signals are broadened drastically (the NMR signals of the solvent are unchanged, thus excluding significant viscosity induced line broadening) and the resonance frequencies for the protons pointing inside the macrocycle are shifted towards high-field as expected for the non-planar conformers.

The coalescence temperature (T_c) is lower than 173 K, but experiments at even lower temperatures are not possible due to the increasing viscosity of the available solvents. Thus, the free activation enthalpy for the flipping process

can only be estimated to be lower than 40 kJ mol^{-1}[13]. This estimation of the maximum free energy of activation shows that the cyclophane **7** is more flexible than calixarenes **1a** with a free energy of activation for the rotation process of the phenylene groups of about 50 kJ mol^{-1}[14]. One explanation for the different flexibilities could be a hindered rotation of the central CH_2- or CHR-links due to steric effects of these groups and hydrogen-bonding between OH-substituents present in the core of the calixarenes.

Crystal Structure and Thermal Properties: An X-ray crystal structure analysis (Table 1) of a single crystal of **7e** obtained from THF revealed that the sulfur atoms are located in a single plane (Figure 1). The unsubstituted *meta*-phenylene subunits are lying on one side of this plane, whereas the substituted ones are on the other side. This conformation can be termed a 1,3-alternate conformation, according to the nomenclature introduced by Gutsche for calixarenes[4]. Thus, the alkyl-substituted benzoyl side groups are pointing away from the macrocyclic core, giving rise to an oval molecular shape. The conformation of the macrocyclic core is similar to that of the unsubstituted parent compound tetrathia[1.1.1.1]metacyclophane[15].

Two molecules of **7e** form a dimer with the central macrocyclic units facing each other and the alkyl chains aligned parallel to each other. The dodecyl substituents of neighboring dimers interdigitate, whereby they assemble in a ribbon-like manner in the direction of the individual molecule's long axis. These ribbons aggregate in one common plane displaced relatively to each other by the length of half a molecule. This structure is reminiscent of a brick wall pattern (Figure 1). In the direction perpendicular to the plane of the macrocycle a tilted columnar arrangement is observed. Additionally, four THF molecules per unit cell fill the space between the alkyl chains (Figure 1).

Compounds **7a-f** show a complex melting behavior as seen in differential scanning calorimetric (DSC) measurements (Figure 2). For **7c**, only a single melting point is observed but, upon heating, **7d−f** show a first melting followed by an exothermic peak. This indicates a transition into a different phase which finally melts into the isotropic liquid. Upon cooling, only **7f** exhibits two reversible phase transitions, which suggests the existence of a stable intermediate phase of **7f**. The first assumption of the existence of a mesophase could not be confirmed by temperature dependent X-ray or solid-state NMR measurements[16], thus the observed complex thermal transformations are interpreted as melting and solidifying through different monotropic crystalline modifications.

Reduction Properties of the Phenylene Sulfide Cyclophane **7** *and Related Model Compounds* **13, 17, 18,** *and* **21**: The generation of species with multiple unpaired electrons is one essential feature[17] to achieve further insight into the magnetic properties of organic systems. The *meta*-phenylene unit has been proven to couple unpaired electrons ferromagnetically in either triplet carbene type species[18] or triphenylmethyl polyradical systems[19]. Recently, we were able to show that also a ketyl-type dianion derived from 3-benzoylbenzophenone **20** (Scheme 4) possesses a triplet ground state due to the paramagnetic coupling of the spins through the *meta*-phenylene unit[20]. Compound **7** comprises two *meta*-benzoylbenzophenone units which are both expected to form a high-spin ground state upon reduction. Thus, **7** is supposed to be an interesting material in the investigation of the interaction between two high-spin systems.

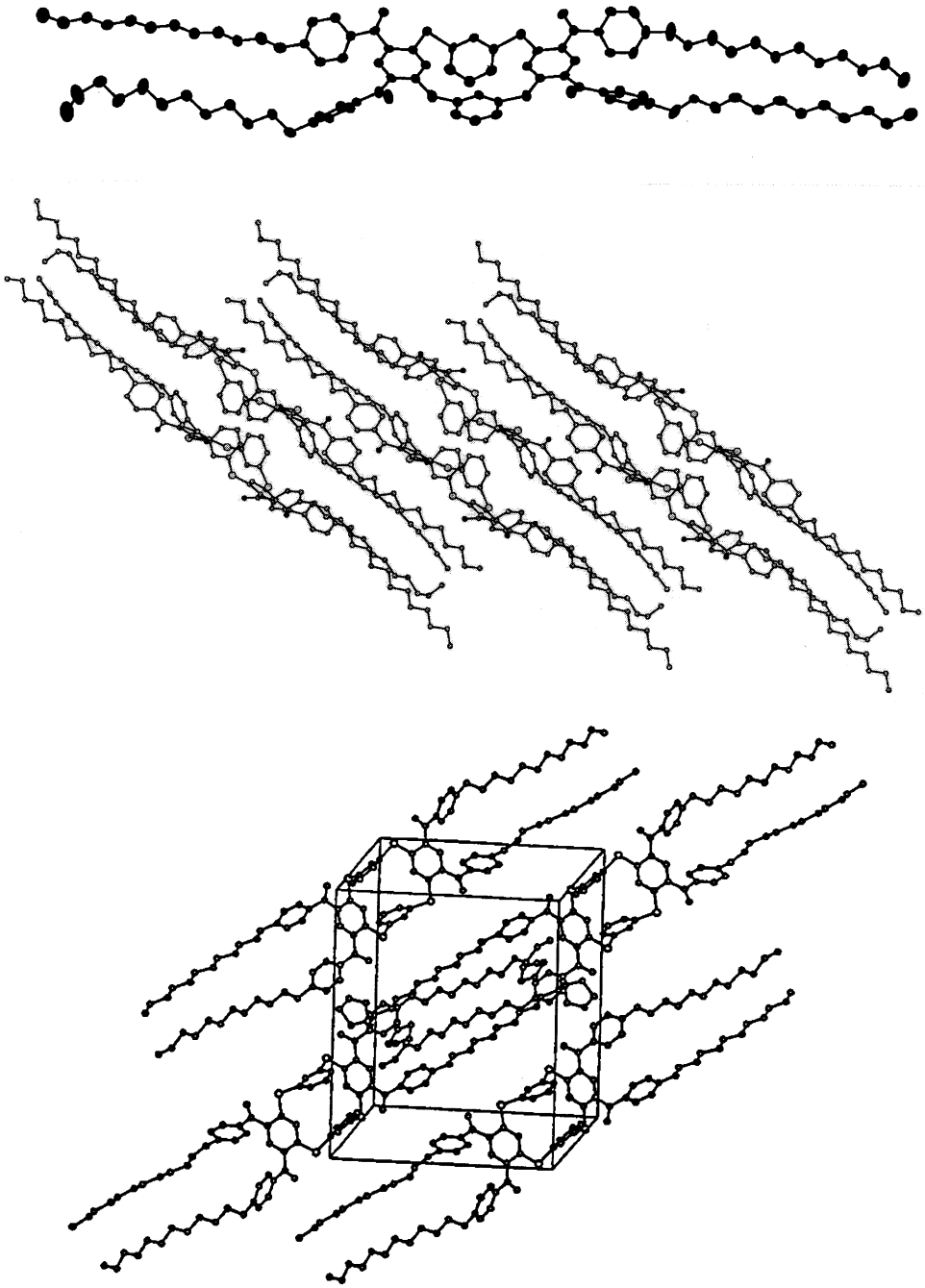
The reduction properties of **7d**, as well as its model compounds **13**, **17** and **18** (Scheme 4), were investigated by cyclic voltammetry (Table 2). Both benzophenones **17** and **18** undergo a reversible one electron reduction, which is facilitated by the phenylthio substituent in comparison to benzophenone (**21**) itself. **17** and benzophenone (**21**) show only an irreversible second electron transfer, while **18** exhibits a reversible second reduction step.

The first reduction of the diketone **13** is facilitated by about 220 mV as compared to benzophenone (**21**). This is due to the combined effects of the second keto group and the phenylthio substituents. The keto group contributes approximately 110 mV, as a comparison of the reduction potential of 4,4′-di-*tert*-butylbenzophenone (**19**) and 4-*tert*-butyl-3-(4′′-*tert*-butylbenzoyl)benzophenone (**20**) reveals. Thus, the phenylthio substituents must be responsible for the other 100 mV. In contrast, the phenylthio substituents do not stabilize the higher charged states as evident when comparing the second reduction potential of **13** with the second reduction potential of **20**.

The macrocycle **7d** undergoes a reversible one electron reduction at a potential similar to that of **13**. Further reduction of **7d** is found as a successive, irreversible, multielectron transfer, occurring 210 mV below the potential of the second reduction of **13**. This finding prompts the assumption that either both diketo sites in **7d** interact strongly or that the 1,3-dibenzoylphenylene subunit is not the actual electrophore. Further insight into the structure of the anionic species has been gained by the EPR spectroscopic analysis described in the next paragraph.

Chemical Reduction and EPR Spectroscopic Characterization of the Metacyclophane and Its Model Compounds: Chemical reductions of the aromatic ketones **7d**, **13**, **17** and **18** were carried out by contacting their tetrahydrofuran solutions with a mirror of sublimed potassium in an EPR tube. Both **17** and **18** form radical anions, whose hyperfine coupling constants were determined by electron nuclear double resonance (ENDOR) experiments at 230 K. The coupling constants were assigned to individual protons by comparison with the benzophenone radical anion[21] (the results are summarized in Table 2). The calculated spin density distributions, derived from Pariser-Parr-Pople (SCF-CI)[22] calculations suggest that the spin density distribution in $\mathbf{17}^{-\bullet}/K^+$ and $\mathbf{18}^{-\bullet}/K^+$ differ essentially (Figure 3). $\mathbf{17}^{-\bullet}$ shows the highest spin density on the outer phenyl ring of the benzophenone moiety, while for $\mathbf{18}^{-\bullet}$, the position of the highest spin resides on the central 1,4-substituted phenylene unit. This behavior can be explained by the influence of the substitution pattern. In either case no evidence was found for a delocalization of the spin density into the phenylthio substituent.

Figure 1. Crystal structure of **7e** (single molecule, band structure, unit cell)



Since ketyl radicals of the benzophenone[23] and fluorenone[24] type are well known to favor alkali metal induced dimerization in frozen solution, leading to a $S = 1$ state with well resolved zero-field splitting components, we studied the frozen solutions of the radical anions of **17** and **18**. The spectra of the monoanion radicals obtained at 135 K in frozen THF matrix are governed by a zero field splitting of $D = 10.3$ mT and a $\Delta m_s = 2$ transition (Figure 4, a). These parameters are typical for triplet species. In the case of the monofunctional compounds **17** and **18** this can only be explained by electronic coupling of the two radical centers by a potassium bridge.

Similar to the radical anions of **17** and **18**, the monoanion radical of **13** exhibits a zero field splitting in frozen solution, typical for biradicals, which can be explained by an association via potassium bridges, similar to the radical anions of **17** and **18**.

Further reduction of $\mathbf{13}^{-\bullet}$ yielded a mixture of the monoanion radical and the dianion diradical. Surprisingly, the fine structure of the experimental spectra obtained in frozen THF matrix can be simulated by a quartet ($S = 3/2$) absorption with the zero-field parameters $D = 5.75$ mT and $E = 0.3$ mT (Figure 4b). Thus, one can conclude that 1:1 ion-pair structures are formed by the association of one

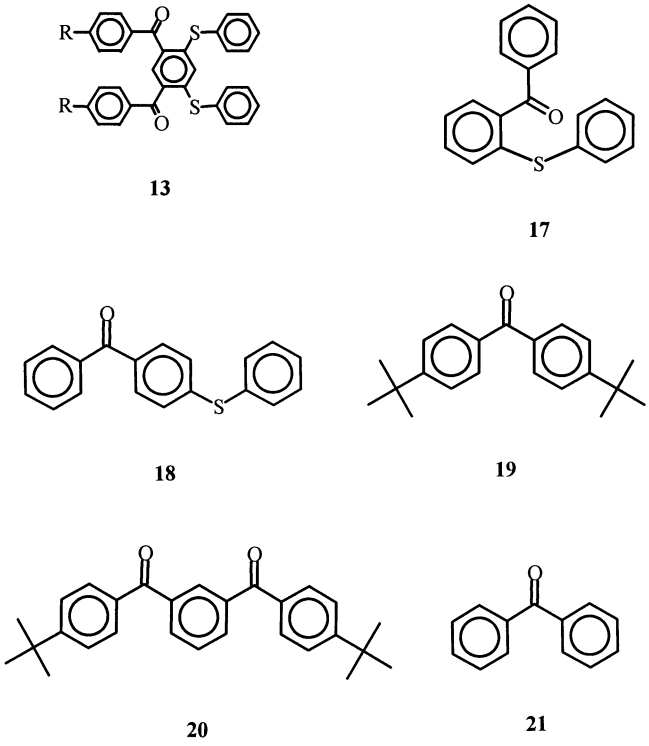
Table 1. Crystallographic data for a single crystal of **7e** grown from THF solution

Space group	$P\bar{1}$
Cell data (standard deviation)	a = 17.821(1) Å b = 14.006(3) Å c = 20.972(1) Å α = 107.549(8)° β = 91.448(6)° γ = 103.688(10)°
Volume	V = 4825.4 Å^3
Number of molecules per unit cell	Z = 4
Density (calcd.)	ρ = 1.048 g·cm^{-3}
Total number of reflections	10790
Observed reflections [$I>6\sigma(I)$]	6123
R factors	R = 0.063; R_w = 0.067 (w = 1)
Temperature	T = 194 K

monoanion radical with one dianion diradical through potassium ions.

The carbonyl groups are the electrophores in all examined model compounds **13**, **17** and **18**. The radical anions are coupled paramagnetically either intra- or intermolecular, thus resulting in organic high-spin molecules with spin multiplicities of up to 3/2[23][24][25]. In contrast, the macrocycle **7d** yielded only one single species upon reduction, which was a monoanion radical characterized by hyperfine coupling constants a_H = 1.58, 1.18, 1.10 and 0.5 mT, derived from high resolution electron-nuclear double-resonance (ENDOR) experiments. The simulated EPR spectrum is in agreement with experimental data, if two equivalent protons are assumed for each coupling constant. A further difference between the model systems and the macrocycle **7d** is the missing association in frozen solution. Moreover, all attempts of further reduction led exclusively to decomposition as shown by cyclic voltammetry. This suggests a different charge distribution in **7d**$^{-\bullet}$ as compared to the ketyl type radicals discussed so far. Additionally, the coupling constants differ from the ones found for the radicals of **13**, **17** and **18**. Therefore, we assume that in the case of **7d** not a ketyl type radical is generated, but the central macrocyclic unit itself is charged. This assumption is also supported by the number of equivalent protons observed in the ENDOR experiments.

Scheme 4. Model compounds for elucidating the reduction properties of **7d**



Moreover, this conjecture is supported by the results of molecular modeling calculations. For the parent compound of the neutral macrocycles, a 1,3-alternate conformation is found, which is in good agreement with the solid state structure of **7e** as well as that of tetrathia[1.1.1.1]metacyclophane[15] itself, thereby proving the reliability of the method. When an extra electron is introduced into the mac-

Figure 2. DSC measurements of **7** with a heating rate of 10 K/min

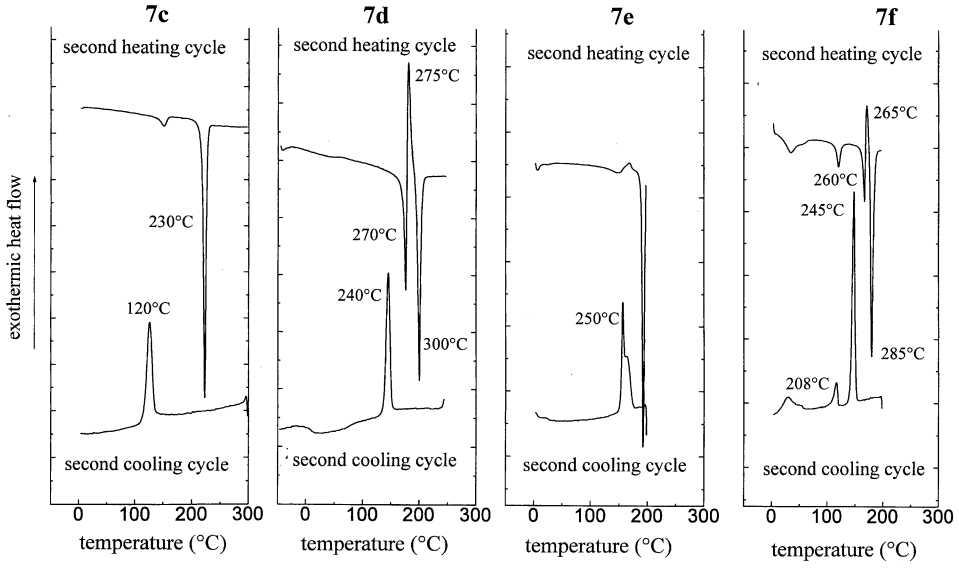
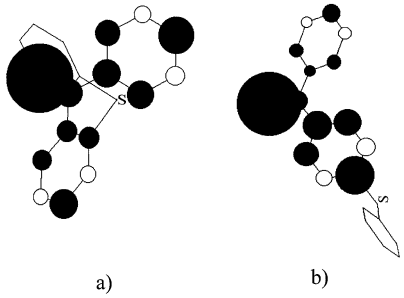


Table 2. Cyclovoltammetric reduction potentials [V][a]

	7d	13	17	18	20	21
$E^1_{1/2}$	−1.85	−1.80	−1.96	−1.90	−1.91	−2.02
$E^2_{1/2}$	−2.50*	−2.29*	−2.57*	−2.44	−2.26	−2.56*
$E^3_{1/2}$		−2.82*			−2.60*	

[a] The asterisk (*) denotes an irreversible reduction, characterized by its cathodic peak potential. Solvent: THF. Conduction salt: Tetrabutylammoniumhexafluorophosphate. Au-electrode versus SCE; T = 253 K

Figure 3. Calculated spin density distributions for **17**$^{-\bullet}$ and **18**$^{-\bullet}$ and ENDOR determined hyperfine coupling constants of the potassium monoanion radicals in THF solution at 243 K (the numbers in parentheses indicate the assignment to the respective protons); unassigned signals correspond to the intensity of one proton



a) b)

	aH [Gauss](assignment)
17$^{-\bullet}$	3.96 (4), 2.92 (4'), 2.75 (2), 1.97 (6,6'), 0.87 (3,5,3'5')
18$^{-\bullet}$	3.26(2'), 2.62 (6'), 2.21 (4), 1.72 (2,6), 0.84, 0.64, 0.53, 0.11
21$^{-\bullet}$	3.50 (4,4'), 2.52 (2,2'6,6'), 0.82 (3,3',5, 5')

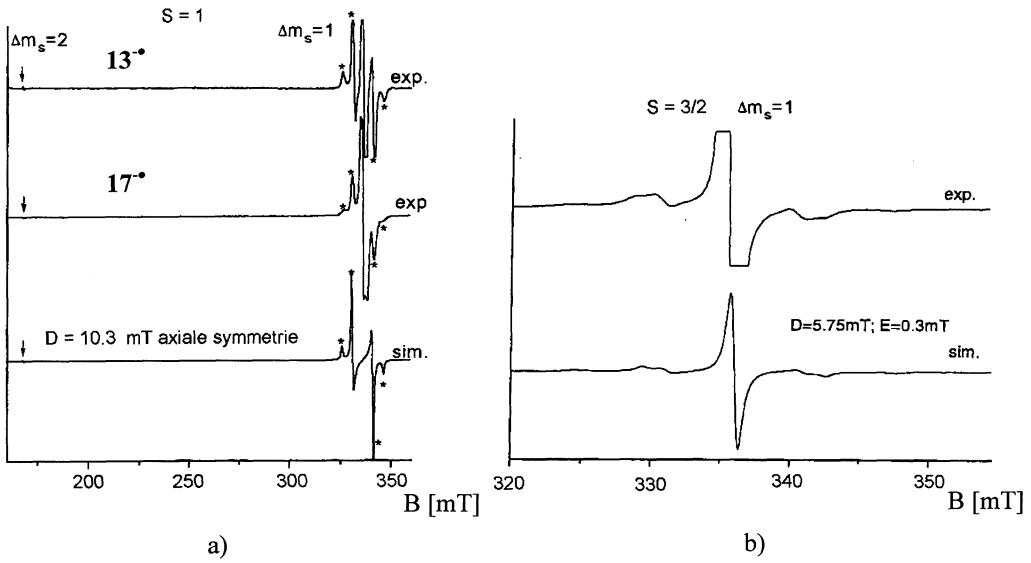
roheterocycle, it adopts a bowl shaped conformation. This provides a host environment for the potassium counterion. One can easily envision a further stabilization of such a complex by chelating the potassium ion through the electron lone pairs of the keto groups. Therefore, due to the host-guest interaction, delocalization of the electron in the macrocyclic unit becomes the preferred process over charging a single keto group.

Conclusion

The nucleophilic aromatic substitution of 1,3-dichlorobenzenes **6** with 1,3-dithioresorcinols **3** provides an easy and high-yield access to sulfur containing, substituted macrocycles. The present nucleophilic aromatic substitution reaction has been found unambiguously to proceed via a reversible polar reaction, thus leading to **7** as the thermodynamically most stable product. Host-guest interaction between the growing phenylene sulfide and alkali metal ions during the generation of the macrocycle provides additional support for the ring closure leading to the remarkable high yields of the cyclophane **7**.

When charging the *meta*-diketo model systems **13** and **17**−**21** (Figure 4), the ketyl groups are the electrophoric groups. In addition to intramolecular spin-spin coupling, the reduced species also show intermolecular spin-spin-coupling via potassium bridges. A different behavior is observed for the tetrathia[1.1.1.1]*meta*-phenylene sulfide **7**. The macrocyclic phenylene sulfide unit is the electroactive unit, due to an intramolecular chelation by the potassium counter ion. This behavior shows the strong host-guest interaction of the sulfur containing macrocycle with metal ions and thus proves its capability in supramolecular chemistry.

Figure 4. a) EPR spectra of **13**$^{-\bullet}$ and **17**$^{-\bullet}$ in THF matrix, potassium counter ion at 135 K, S = 1[a]; b) EPR spectrum of the Δm_s = 1 transition of the mixture of **13**$^{-\bullet}$ and **13**$^{2-\bullet\bullet}$ in THF-maxtrix, potassium counter ion at 135K



[a] The lines denoted with * are due to the triplet species build by association via potassium bridge. The central absorption lines are due to not associated radical anions.

Experimental Section

General: Melting points were determined in open capillary tubes and were not corrected. − Silica Gel "Kieselgel 60, Merck" was used for column chromatography as stationary phase. The eluents are given in the experimental procedures. − Argon was used for preparations under inert gas. − Solvents and starting materials were purified according to standard procedures when necessary. − ^{1}H and ^{13}C-NMR spectra were recorded using a Bruker AC 300 and a Bruker AMX 500. − IR spectra were recorded with a Nicolet FT-IR 320. − Mass spectra were obtained using a Varian CH7A and a VG Instruments ZAB-2.

Differential Scanning Calorimetry: The DSC measurements were carried out on a Mettler DSC 30. The sample was heated in an aluminum pan under nitrogen atmosphere with a rate of 10 K/min.

Temperature-Dependent X-ray Diffraction: The X-ray diffraction patterns were recorded using a Siemens D 500 Kristalloflex with graphite monochromated Cu-K_α radiation, emitted by a rotating RIGAKU RV-300 anode.

Single-Crystal Structure Analysis: The structure determination was carried out on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Cu-K_α radiation. Lattice parameters were estimated by a least-square analysis of 25 reflections with $\theta > 25°$. Intensities were recorded with $\theta/2\theta$ scans. An empirical absorption correction was applied to the data. The structure was solved by direct methods (SIR88) and refined by full matrix least square analysis with anisotropic temperature factors for C, N and O. The hydrogen atoms were refined with isotropic temperature factors in the ridged mode. Pertinent information on the structure determination is given in Table 1. Details about the crystal structure analysis can be obtained from the Fachinformationszentrum Karlsruhe under CSD-408271.

Cyclic Voltammetry: All electrochemical reduction experiments were conducted under an argon atmosphere in THF at 253 K with a gold electrode in the presence of tetrabutylammonium hexafluorophosphate. The measurements were calibrated by an internal ferrocene standard versus saturated calomel electrode. Details are published elsewhere[27].

EPR Experiments: The radical anions were prepared in THF solution on a potassium mirror under high vacuum (10^{-4}−10^{-5} mbar). The EPR/ENDOR spectra were recorded on a Bruker ESP 300 with standard ENDOR unit supply at *x*-band frequency (9.43 GHz) with 100 kHz (EPR cavity) and 12.5 kHz (ENDOR cavity) field modulation, respectively. EPR measurements were performed in liquid and frozen solution (T = 135 K) on a Bruker ESP 300.

3,5,17,19-Tetra(4′-alkylbenzoyl)-1,8,15,22-tetrathia[1.1.1.1]-metacyclophanes **7**.− *General Procedure:* Bis-1,3-(4′-alkylbenzoyl)-4,6-dichlorobenzene (**6**) and an equimolar amount of dithioresorcinol (**3a**) were immersed with two equiv. of potassium carbonate in 30−180 ml of *N*,*N*-dimethylacetamide under an argon atmosphere. This mixture was heated to 100 °C for 6−12 h. After the solution had cooled to r. t., it was poured into the 2.5 fold volume of 10% acetic acid. After 2 h of stirring, the solid was collected by filtration and redissolved in a small amount of dichloromethane. The organic layer was consecutively washed with 10% NaOH solution and water, dried with $MgSO_4$ and evaporated to dryness. The residue was purified by precipitation and/or column chromatography, details of which are given later.

3,5,17,19-Tetrabenzoyl-1,8,15,22-tetrathia[1.1.1.1]metacyclophane (**7a**): The solid product was chromatographed on silica gel with petroleum ether/dichloromethane (1:4). The major fraction was collected and chromatographed once more with ethyl acetate/petroleum ether (1:4) with a gradient ending at 6:1. Finally the product was recrystallized twice from toluene and THF, yielding 1.3 g (27%) of a bright, colorless powder, m.p. 306 °C. − ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 6.76 (2 H, s, H-7,21), 7.39 (2 H, t, ^3J = 7.4 Hz, H-11,25), 7.48 (12 H, m, H-10,12,24,26 and H-3′,5′), 7.59 (4 H, tt, ^3J = 7.4 Hz, ^4J = 1.4 Hz, H-4′), 7.69 (2 H, t, ^4J = 1.4 Hz, H-14,28), 7.71 (2 H, s, H-4,18), 7.83 (8 H, dd, ^3J = 8.5 Hz, ^4J = 1.4 Hz, H-2′,6′). − ^{13}C NMR (75 MHz, *J*-modulated spin-echo experiment, $CDCl_3$, 300 K): δ = 125.8 (C-11,25), 128.4 (C-3′,5′), 129.9 (C-2′,6′), 131.2 (C-7,21), 133.0 (C-4′), 133.7 (C-14,28), 136.4 (C-10,12,24,26), 141.6 (C-4,18) (tertiary aromatic C), 130.4 (C-2,6, 16,20, C-9,13,23,27), 137.1 (C-1′), 145.7 (C-3,5,17,19) (quaternary aromatic C), 194.4 (carbonyl-C). − IR (KBr): $\tilde{\nu}$ = 1649 (carbonyl), 3056 (aromatic CH). − FD-MS; *m*/*z* (%): 849.0 (100) [M^+], 424.8 [M^{2+}]. − $C_{52}H_{32}O_4S_4$ (849.06) found % (calcd. %): C 73.41 (73.56), H 3.90 (3.80), S 15.07 (15.10).

3,5,17,19-Tetra(4′-tert-butylbenzoyl)-1,8,15,22-tetrathia[1.1.1.1]-metacyclophane (**7b**): Purification of the product by washing with acetone yielded 2.1 g (90%) of a colorless powder. − ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 1.35 (18 H, s, CH_3), 6.78 (2 H, s, H-7,21), 7.37 (2 H, t, ^3J = 7.6 Hz, H-11,25), 7.49 (12 H, m, H-10,12,24,26, H-3′,5′), 7.68 (2 H, t, ^4J = 1.6 Hz, H-14,28), 7.72 (2 H, s, H-4,18), 7.808 (8 H, d, ^3J = 8.4 Hz, H-2′,6′). − ^{1}H NMR (500 MHz, [D_8]THF, 223 K): δ = 1.38 (18 H, s (3 Hz), CH_3), 6.84 (2 H, s (1.6 Hz), H-7,21), 7.59 (4 H, dd (3 Hz), ^3J = 7.1 Hz, ^4J = 2.1 Hz, H-10,12,24,26), 7.66 (10 H, m, H-11,25, H-3′,5′), 7.70 (2 H, t, ^4J = 2.1 Hz, H-14,28), 7.80 (2 H, s, H-4,18), 7.90 (8 H, d (2.3 Hz), ^3J = 8.8 Hz, H-2′,6′). − ^{1}H NMR (500 MHz, [D_8]THF, 173 K): δ = 1.35 (18 H, s (15 Hz), CH_3), 6.81 (2 H, s (5 Hz), H-7,21), 7.60 (2 H, s (20 Hz), H10,12,24,26), 7.49 (10 H, s (15 Hz), H-11,25, H-3′,5′), 7.94 (10 H, s (20 Hz), H-4,18, H-2′,6′). − ^{13}C NMR (125 MHz, *J*-modulated spin-echo experiment, $CDCl_3$, 300 K): δ = 31.0 (CH_3), 35.1 (quaternary *t*Bu C), 125.4 (C-3′,5′), 125.8 (C-11,25), 130.1 (C-2′,6′), 130.3 (C-2,6, 14,20), 131.1 (C-7,21), 133.0 (C-9,13,23,27), 133.4 (C-14,28), 134.2 (C-1′), 136.3 (C-10,12,24,26), 141.6 (C-4′), 145.4 (C-3,5,17,19), 157.0 (C-4′), 194.1 (carbonyl-C). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1647 (carbonyl), 2865−2962 (aliphatic CH), 3072 (aromatic CH). − FD-MS; *m*/*z*:1072.7 [M^+].

3,5,17,19-Tetra(4′-n-hexylbenzoyl)-1,8,15,22-tetrathia-[1.1.1.1]-metacyclophane (**7c**): The pure macrocycle was obtained in 85% yield by repeated precipitation from dichloromethane solution with *n*-hexane as a light yellow solid. − ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 0.85 (12 H, t, ^3J = 6.8 Hz, CH_3), 1.28 (24 H, m, CH_2), 1.60 (8 H, m, β-benzylic CH_2), 2.64 (8 H, t, ^3J = 7.7 Hz, benzylic CH_2), 6.73 (2 H, s, H-7,21), 7.25 (8 H, d, ^3J = 8.3 Hz, H-3′,5′), 7.33 (2 H, dd, ^3J = 6.9 Hz, H-11,25), 7.44 (4 H, m, ^3J = 7.0 Hz, H-10,12,24,26), 7.63 (2 H, t, ^4J = 1.6 Hz, H-14,28), 7.65 (2 H, s, H-4,18), 7.74 (8 H, d, ^3J = 8.3 Hz, H-2′,6′); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 13.96 (CH_3), 22.46, 28.86, 30.98, 31.55, (aliphatic C), 35.98 (benzylic C), 125.74 (C-11,25), 128.50 (C-3′,5′), 130.26 (C-2′,6′), 130.59 (C-2, 6, 16,20), 131.10 (C-7,21), 132.96 (C-9,13,23,27), 133.25 (C-14,28), 134.50 (C-1′), 136.26 (C-10,12,24,26), 141.49 (C-11,25), 145.18 (C-3,5,17,19), 149.05 (C-4′), 194.28 (carbonyl-C). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1656 (carbonyl), 2855−2954 (aliphatic CH), 3072 (aromatic CH). − FD-MS; *m*/*z* (%):1184.0 (100) [M^+], 591.95 [M^{2+}]. − $C_{76}H_{80}O_4S_4$ (1185.60): found% (calcd.%): C 76.89 (76.99), H 6.78 (6.80), S 11.32 (10.82).

3,5,17,19-Tetra(4′-n-decylbenzoyl)-1,8,15,22-tetrathia-[1.1.1.1]-metacyclophane (**7d**): The raw material was precipitated from dichloromethane solution with *n*-hexane and was chromatographed on silica gel with petroleum ether/dichloromethane (4:1). This

yielded a light yellow solid, yield 63%. – ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 0.89 (12 H, t, ^3J = 6.8 Hz, CH_3), 1.27 and 1.32 (56 H, m, CH_2), 1.63 (8 H, m, β-benzylic CH_2), 2.67 (8 H, t, ^2J = 7.7 Hz, benzylic CH_2), 6.76 (2 H, s, H-7,21), 7.28 (8 H, d, ^3J = 8.5 Hz, H-3′,5′), 7.36 (2 H, t, ^3J = 7.7 Hz, H-11,25), 7.47 (4 H, m, ^3J = 7.6 Hz, H-10,12,24,26), 7.66 (2 H, s, H-14, 28), 7.68 (2 H, s, H-4,18), 7.77 (8 H, d, ^3J = 8.0 Hz, H-2′,6′). – ^{13}C NMR (125 MHz, *J*-modulated spin-echo experiment, $CDCl_3$, 300 K): δ = 14.1 (CH_3), 22.7, 29.3, 29.5, 29.6, 29.7, 31.2, 31.9 (aliphatic C), 36.1 (benzylic C), 125.8 (C-11,25), 128.6 (C-3′,5′), 130.4 (C-2′,6′), 130.6 (C-2,6,16,20), 131.2 (C-7,21), 133.1 (C-9,13,23,27), 133.4 (C-14,28), 134.6 (C-1′), 136.4 (C-10,12,24,26), 141.6 (C-4,18), 145.3 (C-3,5,17,19), 149.2 (C-4′), 194.9 (carbonyl-C); IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1650 (carbonyl), 2853–2954 (aliphatic CH), 3072 (aromatic CH). – FD MS; *m/z* (%): 1409.0 (100) [M^+], 704.5 [M^{2+}]. – $C_{92}H_{112}O_4S_4$ (1410.0) found% (calcd.%): C 78.28 (78.36), H 8.10 (8.01), S 9.30 (9.10)

3,5,17,19-Tetra(4′-n-dodecylbenzoyl)-1,8,15,22-tetrathia-[1.1.1.1]metacyclophane (**7e**): The pure product was obtained in 81% yield as a colorless solid by successive reprecipitation with acetone or *n*-hexane from dichloromethane solution. Crystallization from THF/petroleum ether yielded crystals of sufficient quality for X-ray structural analysis. – ^{1}H NMR (300 MHz, $CDCl_3$,300 K): δ = 0.89 (12 H, t, ^3J = 6.8 Hz, CH_3), 1.25 (72 H, m, CH_2), 1.60 (8 H, m, β-benzylic CH_2), 2.65 (8 H, t, ^3J = 7.7 Hz, benzylic CH_2), 6.75 (2 H, s, H-7,21), 7.25 (8 H, d, ^3J = 8.3 Hz, H-3′,5′), 7.33 (2 H, t, ^3J = 8.5 Hz, H-11,25), 7.44 (4 H, m, ^3J = 8.5 Hz, H-10,12,24,26), 7.64 (2 H, t, ^4J = 1.6 Hz, H-14,28), 7.66 (2 H, s, H-4,18), 7.74 (8 H, d, ^3J = 8.1 Hz; H-2′,6′); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 14.14 (CH_3), 22.65, 29.31, 29.43, 29.54, 29.60, 29.63, 31.10, 31.88 (aliphatic C), 36.06 (benzylic C), 125.80 (C-11,25), 128.55 (C-3′,5′), 130.32 (C-2′,6′), 130.68 (C-2,6, 16,20), 131.10 (C-7,21), 133.04 (C-9,13,23,27), 133.27 (C-14,28), 134.55 (C-1′), 136.28 (C-10,12,24,26), 141.55 (C-4,18), 145.20 (C-3,5, 17,19), 149.12 (C-4′), 194.33 (carbonyl-C). – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1649 (carbonyl), 2853–2956 (aliphatic CH), 3070 (aromatic CH). – FD MS; *m/z* (%):1522.4 (100) [M^+], 761.3 [M^{2+}]. – $C_{100}H_{128}O_4S_4$ (1522.25): found% (calcd.%): C 78.35 (78.90), H 8.43 (8.47), S 8.48 (8.42)

3,5,17,19-Tetra(4′-n-hexadecylbenzoyl)-1,8,15,22-tetrathia-[1.1.1.1]metacyclophane (**7f**): The raw material was precipitated from dichloromethane solution with acetone or *n*-hexane. Final purification was achieved by column chromatography on silica gel with dichloromethane/petroleum ether (1:4) and yielded 26% of a colorless solid. – ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 0.86 (12 H, t, ^3J = 6.7 Hz, CH_3), 1.24 (104 H, m, CH_2), 1.60 (8 H, m, β-benzylic CH_2), 2.64 (8 H, t, ^3J = 7.7 Hz, benzylic CH_2), 6.73 (2 H, s, H-7,21), 7.25 (8 H, d, ^3J = 8.2 Hz, H-3′,5′), 7.33 (2 H, t, ^3J = 8.5 Hz, H-11,25), 7.44 (4 H, dd, ^3J = 8.5 Hz, ^4J = 1.6 Hz, H-10,12,24,26), 7.63 (2 H, t, ^4J = 1.6 Hz, H-14,28), 7.65 (2 H, s, H-4,18), 7.74 (8 H, d, ^3J = 8.2 Hz; H-2′,6′); ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 14.01 (CH_3), 22.59, 29.26, 29.38, 29.49, 29.60, 31.05, (aliphatic C), 36.00 (benzylic C), 125.74 (C-11,25), 128.48 (C-3′,5′), 130.26 (C-2′,6′), 130.60 (C-2,6, 16,20), 131.05 (C-7,21), 132.99 (C-9,13,23,27), 133.22 (C-14,28), 134.50 (C-1′), 136.23 (C-10,12,24,26), 141.49 (C-4,18), 145.16 (C-3,5, 17,19), 149.05 (C-4′), 194.27 (carbonyl-C). – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1650 (carbonyl), 2851–2956 (aliphatic CH), 3054 (aromatic CH). – FD-MS; *m/z* (%): 1744.6 (100) [M^+], 761.3 [M^{2+}]. – $C_{116}H_{160}O_4S_4$ (1746.8): found% (calcd.%): C 79.82 (79.76), H 9.26 (9.23), S 7.32 (7.34)

14,28-Dimethyl-3,5,17,19-tetra(4′-n-decylbenzoyl)-1,8,15,22-tetrathia-[1.1.1.1]metacyclophane (**7g**): The raw material was precipitated from dichloromethane solution with *n*-hexane and was chromatographed on silica gel with petroleum ether/dichloromethane (4:1). This produced a light yellow solid in 79% yield. – ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 0.86 (12 H, t, ^3J = 6.6 Hz, CH_3), 1.23 and 1.27 (56 H, m, CH_2), 1.57 (8 H, m, β-benzylic CH_2), 2.43 (6 H, s, benzylic CH_3), 2.58 (8 H, t, ^3J = 7.8 Hz, benzylic CH_2), 6.61 (2 H, s, H-7,21), 7.25 (8 H, d, ^3J = 8.1 Hz, H-3′,5′), 7.46 (2 H, t, ^3J = 7.8 Hz, H-11,25), 7.58 (4 H, m, ^3J = 7.8 Hz, H-10,12,24,26), 7.63 (2 H, s, H-4,18), 7.77 (8 H, d, ^3J = 8.1 Hz, H-2′,6′); ^{13}C NMR (125 MHz, *J*-modulated spin-echo experiment, $CDCl_3$, 300 K): δ = 14.2 (CH_3), 16.2 (Ar-CH_3), 22.7, 29.3, 29.5, 29.6, 29.7, 31.2, 31.9 (aliphatic C), 36.1 (benzylic C), 123.1 (C-11,25), 128.4 (C-3′,5′), 130.3 (C-2′,6′), 130.6 (C-2,6, 16,20), 131.2 (C-7,21), 133.7 (C-9,13,23,27), 134.6 (C-1′), 136.3 (C-10,12,24,26), 141.6 (C-4,18), 141.9 (C-14,28), 145.3 (C-3,5, 17,19), 149.2 (C-4′), 194.9 (carbonyl-C). – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1655 (carbonyl), 2849–2955 (aliphatic CH), 3074 (aromatic CH). – FD-MS; *m/z* (%): 1437.8 (100) [M^+], 718.9 [M^{2+}]. – $C_{94}H_{116}O_4S_4$ (1438.1): found% (calcd.%): C 78.50 (78.42), H 8.13 (8.05), S 8.92 (9.01).

Decomposition of **7d** *with Thiophenolate:* 0.564 g (0.400 mmol) of **7d**, 0.176 g (1.600 mmol) of thiophenol and 0.232 g (1.680 mmol) of potassium carbonate were suspended in 20 ml of dry *N,N*-dimethylacetamide under an argon atmosphere. This mixture was heated to 120 °C for 12 h. After the solution had cooled to r. t. it was poured into the 2.5 fold volume of 10% acetic acid. After stirring the suspension for 2 h the solid was collected by filtration and redissolved in dichloromethane. The organic layer was consecutively washed with 10% NaOH solution and water, dried with $MgSO_4$ and evaporated to dryness (0.7 g). The residual product mixture was characterized by FD mass spectrometry. – FD-MS; *m/z* (%): 704.9 (**7d**$^{2+}$, 20%), 782.2 (**13**$^+$, 100%), 1408.9 (**7d**$^+$, 45%), 814.3 (**12**$^+$, 5%), 845.3 (**11**$^+$, 15%), 1487.0 (**10**$^+$, 10%), 1518.2 (**9**$^+$, 10%).

[1] Since the IUPAC nomenclature, denoting **7** as 4,6,16,18-tetrakis(4′-alkylbenzoyl)-2,8,14,20-tetrathiapentacyclo-[19.3.1.13,7.19,13.115,19]octacosa-1(25),3,5,7(28),9,11,13(27),-15,17,19(26),21,23-dodecaene, is rather inconvenient, we have used the nomenclature proposed by Vögtle[8].

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$$\Delta G^{\#} = RT_c \cdot (22.96 + \ln\frac{T_c}{\delta v})$$

The coalescence temperature was too low to be reached and thus no isolated signals for the different conformers could be obtained. Therefore, both, the coalescence temperature and the difference of the resonance frequencies for both conformers, could only be estimated. T_c is lower than 173 K and $\delta\upsilon$ is not smaller than 2 Hz.
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