Pergamon

Tetrahedron, Vol. 52, No. 30, pp. 10043-10052, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00540-6

Chiral Dithia[*n*]paracyclophanes — Synthesis, Crystal Structure, and Chiroptical Properties

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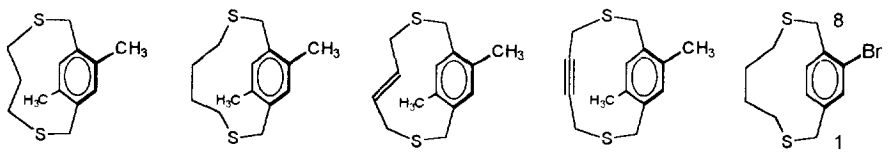
Abstract: The synthesis of the shortly bridged dithia[*n*]paracyclophanes (*n*=7, 8) **1-5** was achieved by the cesium-assisted high-dilution cyclization for the first time. A chiral molecular structure is induced by the pattern of the two methyl substituents. A structure with C_1 symmetry for the dithia[7]paracyclophane **1** is proven by X-ray structure analysis and by low-temperature NMR experiments. The benzene ring is strongly deformed to a boat-shaped conformation. Enantiomeric separation of the cyclophanes **2-5** and the circular dichrograms of the enantiomers are discussed.

Introduction

Paracyclophanes have become important model compounds for the investigation of highly strained and/or deformed ring structures as well as nuclear magnetic resonance phenomena, e.g. deshielding effects.[1] In the course of our studies on structure-chiroptic relationships we are interested in the synthesis, the structure and the chiroptical properties of strained chiral molecules.[2] In this context, shortly bridged [*n*]paracyclophanes like the presented species **1 - 5** are particularly suitable for this purpose.

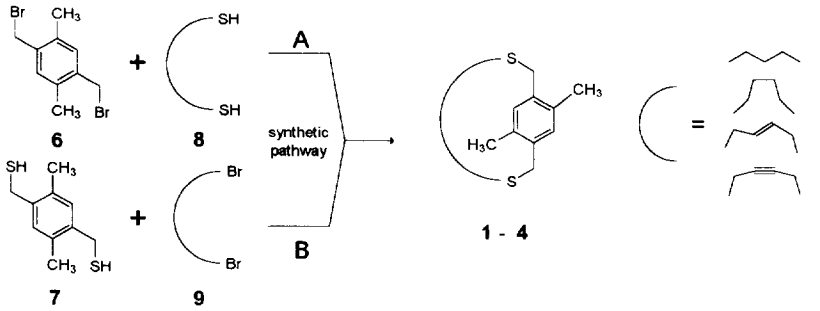


1 **2** **3** **4** **5**

Figure 1: The new planar-chiral dithia[*n*]paracyclophanes **1-5**.

Synthesis

Following the preparation pathway of achiral dithiacyclophanes[3] we reacted the substituted aromatic compounds **6** or **7** with aliphatic dithiols **8** or dibromides **9**. The 1,4-bis(bromomethyl)-2,5-dimethylbenzene (**6**) was easily obtained using phase-transfer-catalyzed bromomethylation according to *Mitchell* et al..[4] The aliphatic dithiols were synthesized from the corresponding 1,ω-dichlorides or dibromides by reaction with thiourea;[5] the dihalides were prepared by nucleophilic substitution from the 1,ω-diols with phosphorus trihalides or thionyl halides.[6] If the dithiol bridge units **8** were unstable or sensitive to the air the aromatic dithiol **7** and a dihalide bridge were used instead.



Scheme 1: General synthesis of the new chiral dimethyldithia[*n*]paracyclophanes **1** - **4**.

The aromatic and the aliphatic building blocks were coupled by cesium-assisted high-dilution cyclization[7] reactions in DMF solution following pathways **A** or **B** (fig. 2). The dithia[*n*]paracyclophanes **2** - **4** were obtained as racemic mixtures in 12 to 53% yield depending on the ring size. The cyclophane **5** was synthesized following pathway A from 2,5-bis(bromomethyl)bromobenzene as the aromatic building block in 50% yield.

The [7]paracyclophane **1** is clamped more shortly than the [8]paracyclophanes **2** - **4**. It was prepared in 4% yield applying analogous conditions and using an ethanol/tetrahydrofuran mixture as the solvent and potassium carbonate as the base.

NMR Spectroscopy

The ^{1}H NMR and the ^{13}C NMR spectra of dimethyldithia[*n*]paracyclophanes indicate the presence of a time averaged C_2 symmetry of the dissolved molecules because conformational motion of their bridge units is fast compared to the NMR time scale. Each signal of the spectrum corresponds to a pair of chemically equivalent protons or carbon atoms due to the molecule's symmetry. Fig 3 shows the ^{1}H NMR spectrum of the 9,12-dimethyl-2,6-dithia[7]paracyclophane (**1**).

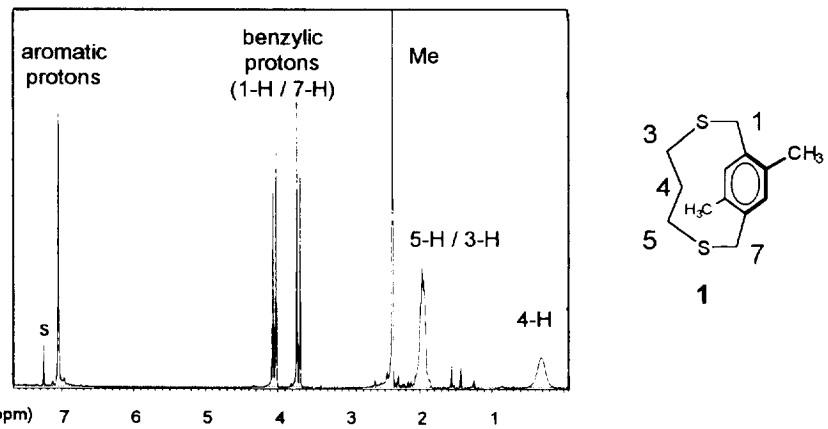


Figure 2: ^{1}H NMR spectrum of the planar-chiral 9,12-dimethyl-2,6-dithia[7]paracyclophane **1** (250 MHz; r.t.; $CDCl_3$; s = solvent).

The signal of the two aromatic protons appears at $\delta = 7.05$. The AB system of the two geminally coupled benzylic pairs of protons at $\delta = 3.71$ and 4.04 indicate that the aliphatic chain is localized on one side of the benzene ring because the flipping movement is hindered. The six methyl protons are observed at 2.38 ppm. The multiplet at ca. 2 ppm is created by the methylene protons of C(3) and C(5) in the propano bridge. The remarkably broad signal at 0.3 ppm can be assigned to the two protons of C(4). The *para* structure and the C_2 molecular symmetry (found in the NMR experiments) indicate that these protons are located directly above the centre of the benzene ring and thus their shifts are strongly affected by the anisotropic effect of the aromatic ring. In fact, the NMR signal shows a high-field shift of about 1.3 ppm with respect to the central methylene group of the corresponding tetrathia cycle (22-membered dimer) which was obtained as byproduct in 50% yield in the synthesis of [7]phane **1**. The high-field shifts observed in dithia[*n*]paracyclophanes are similar to those found for the intraannular protons of [*n*]paracyclophanes.[8]

Unlike the symmetrically substituted [*n*]paracyclophanes **1** - **4** the monosubstituted 10-bromodithia[8]paracyclophane **5** has C_1 symmetry. This is manifested in its ^{1}H NMR spectrum. Diastereotopic benzylic protons act as a probe for the conformational flexibility of a cyclophane bridge because when the bridge is immobilized by a bulky substituent in *ortho* position they create an AB system in the NMR spectrum. The diastereotopic benzylic protons located on C(8) of **5** are represented as such an AB system unlike the benzylic protons on the opposite bridge head that appear as a singlet due to their free movability.

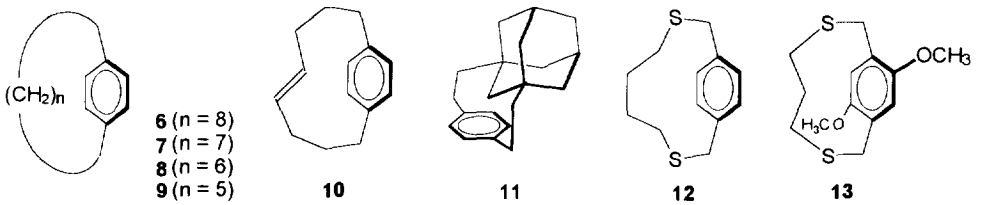


Figure 3: Paracyclophanes **6-13**.

Table 1: ^{1}H NMR shifts of intraannular protons of some [*n*]paracyclophanes and dithia[*n*]paracyclophanes at 293K (* this work; [a] olefinic protons; [b] at 213K).

cyclophane	**1**	**2**	**3**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
δ [ppm]	0.25	0.42	2.50[a]	0.60	0.01	0.2	-0.3	-0.6	1.3[a]	-4.08[b]	0.56	0.42
ref.	*	*	*	*	1	1	1	9	10	11	8	12

Semiempirical geometry optimization with the AM1 Hamiltonian[13] show that the central methylene group can either be directed towards or away from the benzene ring in the dithia[7]paracyclophane **1** assuming a rigid C_2 molecular symmetry. The conformation in which the methylene group points towards the benzene ring is energetically less stable than the other possible conformation. In addition, both C_2-symmetry-based conformations are less favorable than a C_1 symmetry with a zig-zag orientation of the propano bridge (scheme 2).

These theoretical considerations are also supported by a comparison of **1** with the adamantanoparacyclophane **11** that can be formally considered a [7]paracyclophane: In the ^{1}H NMR spectrum of **11** the central methylene group is placed within the anisotropic coil of the aromatic ring experiencing a significant high-field shift ($\delta = -4.08$ ppm at -60°C). In contrast the corresponding methylene protons of **1** appear at $\delta = 0.25$ ppm. Of course, [*n*]paracyclophanes do not have a rigid conformation. The NMR timescale is too slow to distinguish between the various conformations of these molecules so that only an average picture can be observed.

Low-temperature NMR experiments allow to avoid this disadvantage by "deep-freezing" the most stable geometry. In the present investigation of **1** decreasing the temperature reveals for each signal increased splitting as well as doubling (see * in fig. 4). These observations indicate that the most stable configuration has C_1 symmetry with the dithia bridge having C_s symmetry (scheme 2).

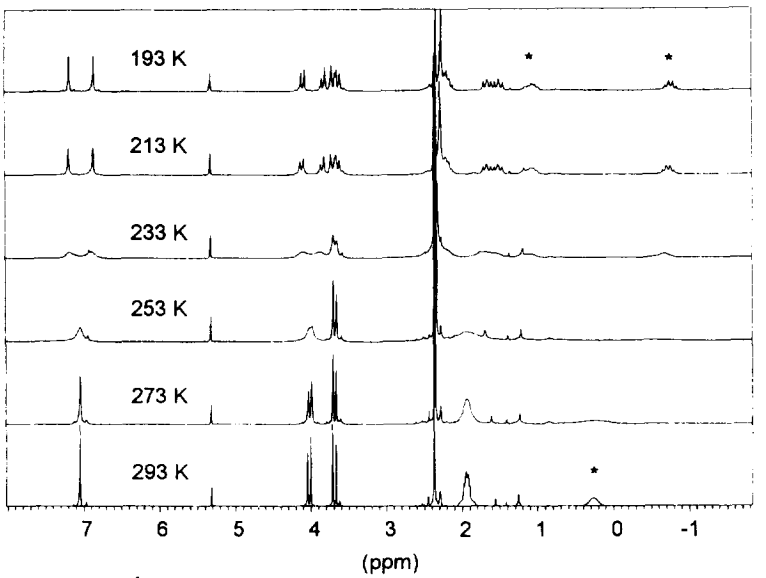
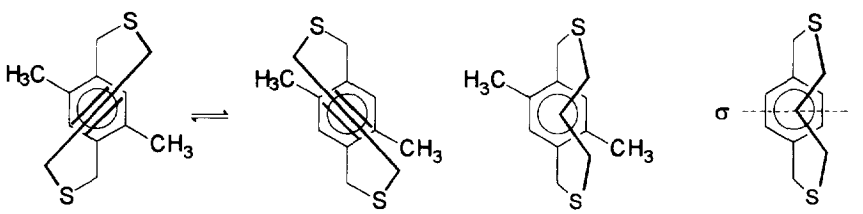


Figure 4: Low-temperature ^1H NMR spectra of the dimethyldithia[7]metacyclophane **1** (250 MHz, CD_2Cl_2).

The free enthalpy of activation for the conformational process $\Delta G_{T_c}^{\neq}$ can be determined with the *Eyring* equation using the experimentally found shift difference $\Delta\nu$ and the coalescence temperature T_c. Thus we obtain a value of 11.6 kcal/mol for the free enthalpy of activation $\Delta G_{T_c}^{\neq}$. This barrier is within the same range as has been found for [8]paracyclophanes.[8]

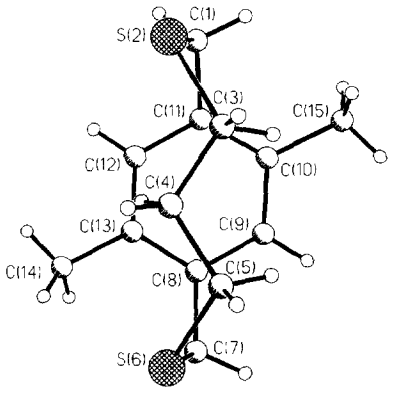
The conformative motion of the bridge unit can be subdivided into two types. 1. Twisting: back-and-forth movement of the sulfur atoms (see scheme 2); 2. Rotation of the methylene groups round about the bond axis.



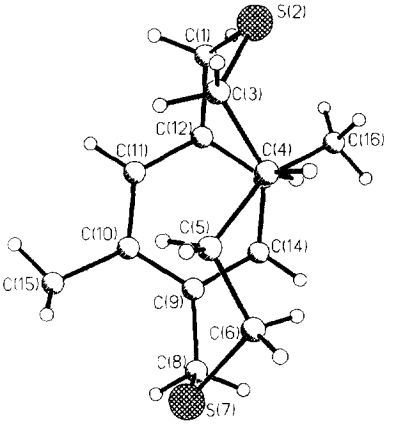
Scheme 2: Twisting as conformative process of **4** and the molecular symmetry of **1** and **14**.

X-ray crystal structures

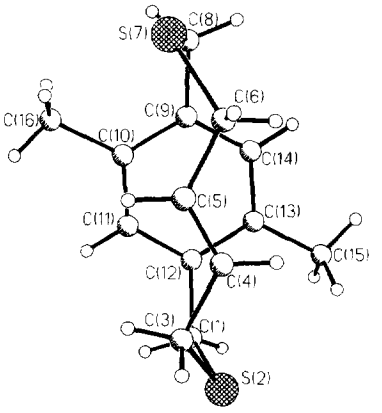
All molecules described (**1** - **5**) have successfully been crystallized and investigated by X-ray crystallography.



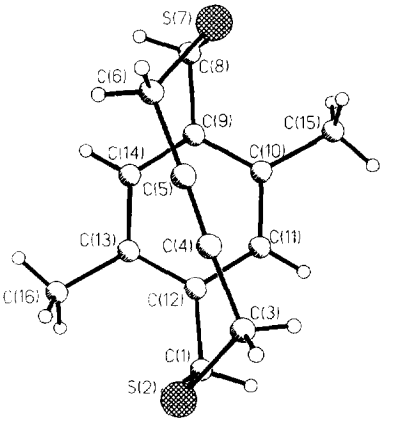
(±)-9,12-dimethyl-2,6-dithia[7]paracyclophane (**1**)



(±)-10,13-dimethyl-2,7-dithia[8]paracyclophane (**2**)



(±)-10,13-dimethyl-2,7-dithia[8]paracyclophan-4-ene (**3**)



(±)-10,13-dimethyl-2,7-dithia[8]paracyclophan-4-yne (**4**)

Figure 5: Crystal structures of the planar-chiral dithia[*n*]paracyclophanes **1-4**.

The chiral dimethyldithia[8]paraphanes possess a crystal structure with C_2 symmetry - as the ^1H and ^{13}C NMR spectra already indicate. With the exception of **1** the sulfur atoms are always directed towards the methyl groups no matter what the hybridization of the bridge carbon atoms is. The C-C single or multiple bonds between the carbon atoms C(4) and C(5) are always located above the center of the aromatic ring. Semiempirical AM1 calculations also predict this geometry to be the most stable one.

Molecular modelling calculations of the [7]paracyclophane **1** show that the C_1 symmetry is approximately 3 kcal/mol more stable than the also imaginable C_2 structure. The seven-membered disulfide bridge causes a strong deformation of the benzene ring which explains the out-of-plane deformation angles $\alpha = 12.1°$ und $\beta = 10.0°$ (table 2).

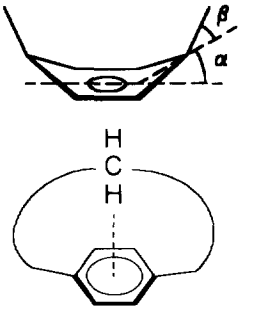
Of the two known dithia[7]paracyclophanes[12,14] (**13** and **14**) only the X-ray crystal structure of the unsubstituted **14** has been described. The molecule shows a remarkable deformation of its benzene ring (α =

11.3° and β = 10.8°). This is in accordance with the deformation angles found in the X-ray structure analysis of the new dithia[7]cyclophane **1** (α = 12.1° and β = 10.0°).

[*n*]Paracyclophanes as well as [*n*]metacyclophanes are the more deformed towards a boat-shaped conformation the shorter their bridge lengths get (out-of-plane deformation angle α). The α carbon atoms form an additional out-of-plane deformation angle β (table 2).

Table 2: Out-of-plane deformation angles α and β as well as the distance between the nearest intraannular proton and the centre of the benzene ring ($d_{H\text{-}arene}$) of the dithia[*n*]paracyclophane **1** - **5** and **14** (*this work).

[*n*]PCP	α [°]	β [°]	$d_{H\text{-}arene}$ [Å]	ref.
1	12.1	10.0	3.07	*
1 (AM1)	17.5	11.2	-----	*
14	11.3	10.9	-----	14
2	8.4	5.5	2.76	*
3	6.4	5.4	2.28	*
4	6.6	7.9	-----	*
5	9.1	9.2	2.79	*



Inspection of the out-of-plane deformation angles in the series **2**-**4** shows no simple relationship between bridge lengths and deformation angles. Although the largest deformation angles are observed in the molecule with the shortest bridge (α+β=14.5° in molecule **4**) the second largest deformation angle is found in the species with the longest bridge, paracylophane **2**. This can only be rationalized by the steric demand of the higher number of hydrogens in the butano bridge that force the bridge into a zig-zag rather than an elongated conformation. Similar considerations are also true for the buteno-bridged cyclophane **3**.

Separation of enantiomers and chiroptics

Unlike the dithia[*n*]metacyclophanes[15] the racemates of the new dithia[*n*]paracyclophanes **1**-**4** can efficiently be separated into enantiomers using cellulose-tris(3.5-dimethylphenylcarbamate) (CDMPC)[16] as the chiral stationary phase and *n*-hexane:isopropanol (9:1) as the eluent (separation factors α up to 3.17 and resolutions R up to 7.40!). On-line control of the optical rotation allows the assignment of the two enantiomers. The concentration can be determined UV spectroscopically or indirectly by GC measurements.

Measurement of the circular dichrogramms was carried out in *n*-hexane or acetonitrile as the solvent. Fig. 6 shows the circular dichrogramms of the dithia[*n*]paracyclophanes **1** - **4**.

Exact assignment of the Cotton effects of the shown circular dichrogramms can only be achieved by comparison with calculated UV and CD data, because they are a result of the superposition of the single structural elements, e.g. thioether and benzene chromophore. The C-C multiple bonds do not contribute to the CD spectra in the range of 185 - 350 nm as they do not absorb above 185 nm. Experimentally determined CD bands could be assigned to the electronic transitions by rough CD calculations as compiled in table 3.

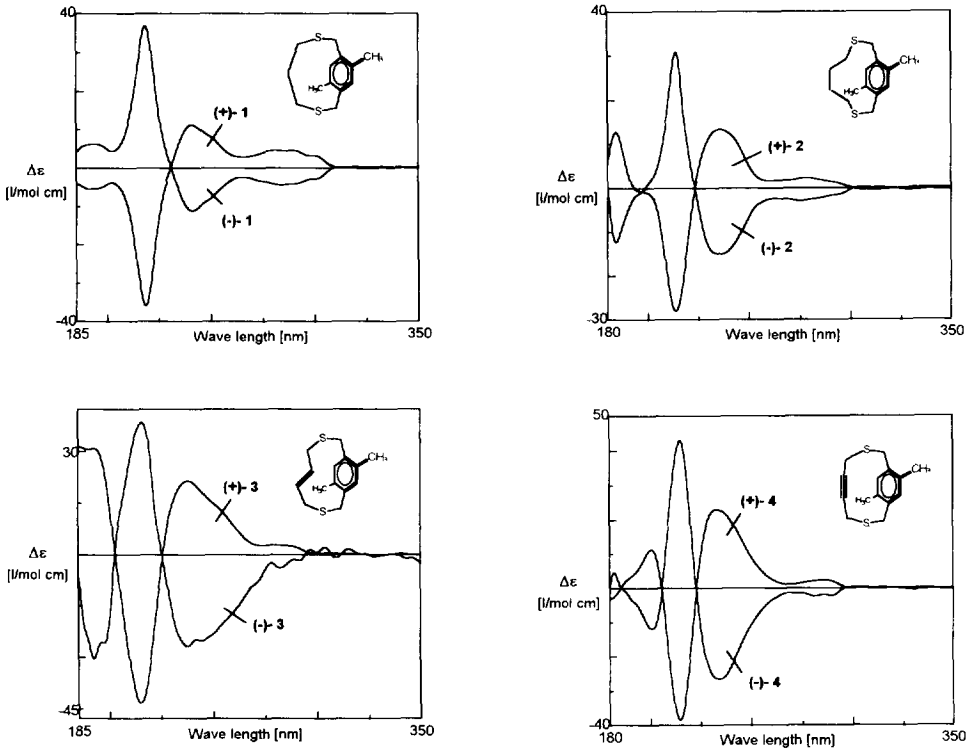


Figure 6: Circular dichrogramms of the new dithia[*n*]paracyclophane **1** - **4**.

Table 3: Assignment of the Cotton effects to their corresponding electronic transition

CD-band (λ_{max} [nm])	CD-sign[a]	assigned transition
270-310	positive	$\pi\,\pi^*$ (benzene) and lone pair (S) $\rightarrow \sigma^*/\pi^*$
230-270	positive	$\pi\pi^*$ (L_a)
205-230	negative	$\pi\pi^*$ (benzene)
<205	positive	$\pi\pi^*$ (benzene)

[a]the first Cotton effect is arbitrarily a positive one; because the absolute configuration is unknown no correlation to one of the enantiomers is possible.

Furthermore all measured CD spectra show resemblance with recently investigated dithia-metacyclophanes[2] so that we expect similar electronic transitions to be important here. We expect that a mixture of the different dithia[*n*]paracyclophane conformers contributes to the shape of the CD spectra as has already been shown in the case of the dithia[*n*]metacyclophanes.[2] As discussed for the NMR spectroscopical results [*n*]paracyclophanes have two conformers that result from the "twisting" process. These conformers give unlike those of the [*n*]metacyclophanes almost identical CD spectra with equal signs. The conformers can be assumed to be present in equal amounts due to their similar stability which has to be taken into account in the CD calculation. The barrier of the conformational transformation is low (*vide supra*).

In contrast to the CD spectrum of [*n*]metacyclophanes,[2,15] that experiences a strong impact of the dithia bridges, the circular dichrograms of [*n*]paracyclophanes are only mildly influenced by the conformations of the dithia bridge unit. Hence, the Cotton effects of the latter is almost solely created by the asymmetrically distorted benzene chromophore.

EXPERIMENTAL

General: Column chromatography was performed using Merck Kieselgel 60 70-230 Mesh, TLC on aluminium sheets coated with Kieselgel 60 F_{254}. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM 250 (^1H NMR 250 MHz, ^{13}C: 62.9 MHz and Varian EM 360 (60 MHz) using the solvent as internal standard. GC-MS spectra were recorded on a Hewlett Packard HP 5890 II/HP 5989 A. Enantiomeric separation was achieved by HPLC: Gilson Serie Abimed; column: (Cellulose tris(3,5-dimethylphenylcarbamate), column dimension: 500 x 4.6 mm, eluent: *n*-hexane/*iso*propanol 9:1; flow: 0.5 ml min^{-1}; pressure: 3 bar; 25°C; detection: UV, λ = 254 nm). Melting points are uncorrected.

1,4-Bis(bromomethyl)-2,5-dimethylbenzene (6): A stirred mixture of 53.0 g (500 mmol) 1,4-dimethylbenzene, 250 ml hydrobromic acid (48%), 70 ml glacial acetic acid, 30.0 g (1 mol) trioxane, and 2.5 g tetradecyltrimethylammonium bromide was heated under reflux for 24 h. After cooling down to 20°C the colorless crystalline material was filtered off, washed with water, and recrystallized from chloroform/ethanol 1:1 to yield 97,0 g (66%) of **6**: mp 160°C; ^1H NMR (60 MHz, $CDCl_3$): δ 2.4 (s, 6H, CH_3), 4.6 (s, 4H, $ArCH_2Br$), 7.3 (s, 1H, ArH); GC-MS m/z = 292 (M^+ [$C_{10}H_{12}Br_2$], 8%), 213 (M^+-Br, 57%), 132 (M^+-2Br, 100%), 117 (132-CH_3, 9%), 91 (C_7H_7, 30%), 64 (C_5H_4, 20%), 51 (C_4H_3, 10%); DC: (SiO_2): R_f = 0.78 (dichloromethane/petrolether 40/60 (1:1)).

1,4-Bis(mercaptomethyl)-2,5-dimethylbenzene (7): A stirred mixture of 14.6 g (50 mmol) 1,4-bis(bromomethyl)-2,5-dimethylbenzene, 8.35g (0.11 mol) thiourea, and 25 ml ethanol (95%) was heated under reflux for 5 h. Then 60 ml of sodium hydroxide solution (20%) was added and heated for additional 5 h. The cold reaction mixture was acidified with hydrochloric acid (18%), the mercaptane layer was separated, the water layer extracted with dichloromethane and the combined organic layers dried over $MgSO_4$. The solvent was evaporated to yield the foul-smelling mercaptane, which was stored under inert gas in a refridgerator: 6.7 g (68%); ^1H NMR (60 MHz, $CDCl_3$): δ 1.62 (t, 2H, J = 7 Hz, SH), 2.37 (s, 6H, CH_3), 3.77 (d, 4H, J = 7 Hz, $ArCH_2SH$), 7.15 (s, 2H, ArH); GC-MS m/z = 198 (M^+ [$C_{10}H_{14}S_2$], 41%), 165 (M^+-SH, 100%), 132 (M^+-2 SH, 72%), 91 (C_7H_7, 30%),77 (C_6H_5, 15%), 65 (C_5H_5, 16%), 51 (C_4H_3, 13%).

(±)-9,12-Dimethyl-2,6-dithia[7]paracyclophane (1): To a stirred suspension of 5 g K_2CO_3 in 350 ml methanol was added a solution of 5 mmol 1,4-bis(bromomethyl)-2,5-dimethylbenzene and 5 mmol 1,3-dimercaptopropane dissolved in 150 ml tetrahydofuran/ethanol (2:1) over 12h using a medical perfusor under reflux. Usual work-up as described below: colorless crystals; 0.05 g (4%); (SiO_2): R_f = 0.52; mp 97°C (*n*-hexane/acetone); ^1H NMR (250 MHz, $CDCl_3$): δ 0.31 (br, 2H, CH_2), 1.85-2.10 (m, 4H, CH_2), 2.38 (s, 6H, CH_3), 3.71 (d, 2H, J = 11.6 Hz, $ArCH_2S$), 4.04 (d, 2H, J = 11.6 Hz, $ArCH_2S$), 7.05 (s, 2H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 18.85 ($2CH_3$), 29.63 (CH_2), 34.38 ($2CH_2$), 34.53 (2C, $ArCH_2S$), 132.96 (2CH), 135.20 ($2C_q$), 136.01 ($2C_q$); GC-MS m/z = 238 (M^+ [$C_{13}H_{18}S_2$], 12%), 132 (M^+-$S(CH_2)_3S$, 100%), 117 (132 - CH_3, 13%), 91 (C_7H_7, 11%), 77 (C_6H_5, 3%), 65 (C_5H_5, 3%), 51 (C_4H_3, 3%); calcd. C 65.49 H 7.61, found: C 65.78 H 7.83; enantio. sep.: t_r [$(-)_D$-**1**] = 22 min; t_r [$(+)_D$-**1**] = 31 min; k' [$(-)_D$-**1**] = 0.69; k' [$(+)_D$-**1**] = 1.38; α = 2.01; R = 2.57.

X-ray Structure: Crystal data: $C_{13}H_{18}S_2$, MW 238.4 g mol^{-1}, colorless crystals, dimensions 0.90 x 0.65 x 0.55 mm, ρ_{calc} = 1.26 g cm^{-3}, triclinic, space group $P\bar{1}$ (No.2), a = 6.802(3), b = 7.546(3), c = 13.742(5) Å, α = 75.99(3)°, β = 82.08(3)°, γ = 66.62(3)°, V = 627.5(4) $Å^3$, Z = 2, F(000) = 256. A total of 2943 reflections were recorded on a Nicolet R3m diffractometer (graphite monochromator, λ (Mo-K_α) = 0.71073 Å, μ(Mo-K_α) = 0.39 mm^{-1}) at T = 293(2) K. Of these, 2828 independent reflections were used for the structure solution (SHELXTL-Plus[17]) and refinement (138 parameters, SHELXL-93[18]). Non-hydrogen atoms were refined anisotropically (full-matrix least-squares refinement on F^2); H atoms were refined using a riding model, wR2 = 0.110 (R for F>4σ(F) = 0.037). Largest difference peak 0.27 e$Å^{-3}$.

General procedure of the syntheses of **2-5**: To a stirred suspension of 5.0 g Cs_2CO_3 in 500 ml dry and degassed DMF was added simultaneously 5 mmol 1,4-bis(bromomethyl)- or 1,4-bis(mercaptomethyl)-2,5-

dimethylbenzene (or 2,5-bis(bromomethyl)bromobenzene for **5**) and 5 mmol α,ω-dimercaptoalkane or 1,4-dibromobutene (-butyne) each dissolved in 50 ml DMF over 17h using a medical perfusor at rt. After additional stirring for 5h the solvent was evaporated, treated with water and dichloromethane. The organic extract was washed with water and dried over Na_2SO_4. Purification by silica-gel column chromatography (dichloromethane/petrolether 40/60 (1:1)).

(±)-10,13-Dimethyl-2,7-dithia[8]paracyclophane (2): 0.55 g (44%); (SiO_2): R_f = 0.58; mp 74°C (acetone); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.42 (m, 2H, CH_2), 1.00 (m, 2H, CH_2), 1.86 (m, 2H, CH_2), 2.14 (m, 2H, CH_2), 2.40 (s, 6H, CH_3), 3.66 (d, 2H, J = 12.3 Hz, $ArCH_2S$), 3.90 (d, 2H, J = 12.3 Hz, $ArCH_2S$), 6.94 (s, 2H, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 18.59 (2C, CH_3), 28.44 (2C, CH_2), 31.32 (2C, CH_2), 34.65 (2C, $ArCH_2S$), 132.98 (2CH), 135.00 ($2C_q$), 135.45 ($2C_q$); GC-MS m/z = 252 (M^+ [$C_{14}H_{20}S_2$], 23%), 164 (M^+-SBu, 2%), 132 (M^+-SBuS, 100%), 117 (132-CH_3, 15%); calcd. C 66.61 H 7.99.found: C 66.27 H 7.81; enantio. sep.: t_r [(-)$_D$-**2**] = 25 min; t_r [(+)$_D$-**2**] = 46 min; k' [(-)$_D$-**2**] = 0.92; k' [(+)$_D$-**2**] = 2.54; α = 2.76; R = 5.25.

X-ray Structure: Crystal data: $C_{14}H_{20}S_2$, MW 252.4 g mol^{-1}, colorless prisms, dimensions 0.55 x 0.30 x 0.20 mm, $\rho_{calc.}$ = 1.24 g cm^{-3}, monoclinic, space group $P2_1/c$ (No.14), a = 14.068(1), b = 7.176(1), c = 13.875(1) Å, β = 104.28(1)°, V = 1357.4(2) Å^3, Z = 4, F(000) = 544. A total of 2101 reflections were recorded on an Enraf-Nonius CAD4 diffractometer (graphite monochromator, λ (Cu-K$_\alpha$) = 1.54178 Å, μ(Cu-K$_\alpha$) = 3.30 mm^{-1}) at T = 200(2) K. Of these, 1998 independent reflections were used for the structure solution (SHELXTL-Plus[17]) and refinement (147 parameters, SHELXL-93[18]). Non-hydrogen atoms were refined anisotropically (full-matrix least-squares refinement on F^2); H atoms were refined using a riding model, wR2 = 0.118 (R for F>4σ(F) = 0.043). Largest difference peak 0.38 eÅ^{-3}. An absorption correction on the basis of Ψ-scans was applied.

(±)-10,13-Dimethyl-2,7-dithia[8]paracyclophan-4-ene (3): 0.155 g (12%); (SiO_2): R_f = 0.64; mp 122°C (acetone): ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.40 (s, 6H, CH_3), 2.50-2.60 (m, 2H , CH_2), 2.80-2.89 (m, 2H, CH_2), 3.67 (d, 2H, J = 12.4 Hz, $ArCH_2S$), 3.82 (d, 2H, J = 12.4 Hz, $ArCH_2S$), 4.27-4.32 (m, 2H, HC=C), 6.72 (s, 2H, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 18.31 (2C, CH_3), 32.40 (2C, CH_2), 34.35 (2C, $ArCH_2S$), 128.43 (2C, C=C), 132.01 (2C, CH), 134.81 ($2C_q$), 136.41 ($2C_q$); GC-MS m/z = 250 (M^+ [$C_{14}H_{18}S_2$], 25%), 164 (M^+-SBu, 8%), 132 (M^+-SBuS, 100%), 117 (132-CH_3, 13%); calcd. C 67.15 H 7.24, found: C 67.14 H 7.23; enantio. sep.: t_r [(-)$_D$-**3**] = 30 min; t_r [(+)$_D$-**3**] = 67 min; k' [(-)$_D$-**3**] = 1.31; k' [(+)$_D$-**3**] = 4.15; α = 3.17; R = 7.40.

X-ray Structure: Crystal data: $C_{14}H_{18}S_2$, MW 250.4 g mol^{-1}, colorless prisms, dimensions 0.43 x 0.40 x 0.20 mm, $\rho_{calc.}$ = 1.27 g cm^{-3}, triclinic, space group $P\bar{1}$ (No.2), a = 6.896(1), b = 7.389(1), c = 14.113(1) Å, α = 99.60(1)°, β = 96.58(1)°, γ = 109.61(1)°, V = 656.2(2) Å^3, Z = 2, F(000) = 268. A total of 2745 reflections were recorded on an Enraf-Nonius CAD4 diffractometer (graphite monochromator, λ (Cu-K$_\alpha$) = 1.54178 Å, μ(Cu-K$_\alpha$) = 3.42 mm^{-1}) at T = 208(2) K. Of these, 2477 independent reflections were used for the structure solution (SHELXTL-Plus[17]) and refinement (148 parameters, SHELXL-93[18]). Non-hydrogen atoms were refined anisotropically (full-matrix least-squares refinement on F^2); H atoms were refined using a riding model, wR2 = 0.139 (R for F>4σ(F) = 0.050). Largest difference peak 0.66 eÅ^{-3}. An absorption correction on the basis of Ψ-scans and an extinction correction were applied.

(±)-10,13-Dimethyl-2,7-dithia[8]paracyclophan-4-yne (4): 0.195 g (16%); (SiO_2): R_f = 0.52; mp 149°C (acetone); ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.37 (s, 6H, CH_3), 2.87 (d, 2H, J = 16.3 Hz, $SCH_2C\equiv$), 3.02 (d, 2H, J = 16.3 Hz, $SCH_2C\equiv$), 3.70 (d, 2H, J = 12.7 Hz, $ArCH_2S$), 3.93 (d, 2H, J = 12.7 Hz, $ArCH_2S$), 6.81 (s, 2H, ArH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.22 (2C, CH_3), 19.41 (2C, CH_2), 35.81 (2C, $ArCH_2S$), 77.58 (2C, C≡C), 132.08 (2C, ArCH), 134.53 ($2C_q$), 135.78 ($2C_q$); GC-MS m/z = 248 (M^+ [$C_{14}H_{16}S_2$], 85%), 215 (M^+-SH, 53%), 202 (M^+-SCH_2, 38%), 187 (202-CH_3, 35%), 132 (M^+-SC_4H_4S, 100%), 117 (132-CH_3, 53%); calcd. C 67.69 H 6.49, found: C 67.39 H 6.54.

X-ray Structure: Crystal data: $C_{14}H_{16}S_2$, MW 248.4 g mol^{-1}, colorless plates, dimensions 0.45 x 0.40 x 0.10 mm, $\rho_{calc.}$ = 1.31 g cm^{-3}, monoclinic, space group $P2_1/c$ (No.14), a = 8.774(3), b = 20.897(9), c = 7.567(3) Å, β = 114.42(3)°, V = 1263(1) Å^3, Z = 4, F(000) = 528. A total of 2382 reflections were recorded on a Nicolet R3m diffractometer (graphite monochromator, λ (Mo-K$_\alpha$) K$_\alpha$)= 0.71073 Å, μ(Mo-K$_\alpha$) = 0.39 mm^{-1}) at T = 293(2) K. Of these, 2232 independent reflections were used the the structure solution (SHELXTL-Plus[17]) and refinement (147 parameters, SHELXL-93[18]). Non-hydrogen atoms were refined anisotropically (full-matrix least-squares refinement on F^2); H atoms were refined using a riding model, wR2 = 0.084 (R for F>4σ(F) = 0.033). Largest difference peak 0.26 eÅ^{-3}.

(±)-10-Bromo-2,7-dithia[8]paracyclophane (5): 0,75 g (50%); (SiO_2): R_f = 0.52; mp 92°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.60 (m, 1H, CH_2), 0.79-0.92 (m, 3H, CH_2), 1.94-2.23 (m, 4H, CH_2), 3.70 (d, 1H, J = 12.4 Hz, $ArCH_2S$), 3.71 (s, 2H, $ArCH_2S$), 4.14 (d, 1H, J = 12.4 Hz, $ArCH_2S$), 7.22 (dd, 1H, ^{3}J = 7.9 Hz, ^{4}J = 1.4 Hz, ArH-13), 7.27 (d, 1H, ^{3}J = 7.9 Hz, ArH-14), 7.53 (d, 1H, ^{4}J = 1.4 Hz, ArH-11); ^{13}C NMR (100.9 MHz,

$CDCl_3$): δ 28.60 (2C, CH_2), 30.24 (1C, CH_2), 30.44 (1C, CH_2), 36.48 (1C, $ArCH_2S$), 36.90 (1C, $ArCH_2S$), 125.18 ($1C_q$), 129.19 (1CH), 131.71 (1CH), 134.71 (1CH), 136.98 ($1C_q$), 140.01 ($1C_q$); GC-MS m/z = 304 (M^+ [$C_{14}H_{15}S_2Br$], 4%), 223 (M^+-Br, 1%), 182 (M^+-Br-SBuS, 54%), 120 (95%), 55 (100%); calcd. C 47.53; H 4.99, found: C 47.40; H 4.99.

X-ray Structure: Crystal data: $C_{12}H_{15}BrS_2$, MW 303.3 g mol^{-1}, colorless prisms, dimensions 0.35 x 0.30 x 0.20 mm, ρ_{calc} = 1.61 g cm^{-3}, monoclinic, space group $P2_1/c$ (No.14), a = 13.048(1), b = 7.958(1), c = 12.208(1) Å, β = 99.38(1)°, V = 1250.7(3) $Å^3$, Z = 4, F(000) = 616. A total of 3573 reflections were recorded on an Enraf-Nonius CAD4 diffractometer (graphite monochromator, λ (Cu-K_α) = 1.54178 Å, μ(Cu-K_α) = 7.30 mm^{-1}) at T = 223(2) K. Of these, 2121 independent reflections were used the the structure solution (SHELXTL-Plus[17]) and refinement (136 parameters, SHELXL-93[18]). Non-hydrogen atoms were refined anisotropically (full-matrix least-squares refinement on F^2); H atoms were refined using a riding model, wR2 = 0.159 (R for $F>4\sigma(F)$ = 0.056). Largest difference peak 1.05 e$Å^{-3}$. An absorption correction on the basis of Ψ-scans was applied.

Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Centre, 12 Union Road, GB-Cambridge CB2 1EZ, on quoting the complete journal citation.

Acknowledgement: This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 334). We thank Dr. S. Grimme for calculations and discussions.

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(*Received in Germany* 22 *April* 1996; *accepted* 5 *June* 1996)