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Paracyclophanes: Extending the Bridges. Synthesis[‡]

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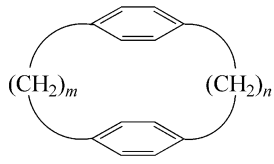
Preparatively satisfactory routes to [3.2]paracyclophane (**10**), [4.2]paracyclophane (**14**), [4.3]paracyclophane (**19**) as well as several derivatives of these compounds – among others the bromides **25**, the ester **31**, the diesters **40**–**43** – are described using well-established methods of cyclophane chemistry (ring-closure reactions leading to thiacyclophanes, ring contraction by sulfone pyrolysis). The parent systems and their derivatives are now available in gram quantities allowing a study of their chemical properties.

Introduction

Since the serendipitous discovery of [2.2]paracyclophane (**1**, $m = n = 2$) by Brown and Farthing 60 years ago[2] and the deliberate development of this area of aromatic chemistry by Cram and his students[3] during the 1950ies and 60ies this class of layered compounds has fascinated numerous research groups.[4] Many important discoveries were made along a route to increasingly complex structures and more and more practical applications of a group of compounds, which originally were available in minute amounts only, have been reported. Still, looking back from the height reached by this chemical sexagenarian, knowledge gaps are also clearly visible. These have not only to do with still unknown representatives in a series of homologs and analogs (see below) but – in particular – with little knowledge about the chemical properties of individual members of the [*m.n*]-cyclophanes series. In the often fierce race to prepare a particular cyclophane, the emphasis often was more on being first than to study the chemical properties of the presumably "interesting" or even "esthetically pleasing" target molecules. But besides having novel and surprising structural properties – which often is the case for [*m.n*]paracyclophanes – it is the chemical properties of compounds that make them "interesting". To learn about chemical behavior the prerequisite is substrate availability, i.e. preparatively satisfactory routes to sufficient amounts of starting material, meaning at least gram amounts. This condition is only fulfilled for a small number of the hydrocarbons **1** collected in Scheme 1, a summary of the [*m.n*]paracyclophanes with up to $m = n = 4$ known today.[5]



1

n \ *m*	0	1	2	3	4
0	(+)[6]	–[8]	–	–	–
1	+[8]		–[4]	–[10]	–[10]
2	–	+[4]		+[4]	+[11]
3	–	–[10]	+[4]		+[4,12]
4	–	–[10]	+[11]	+[4,12]	

+ = known compound
– = unknown compound

Scheme 1. The [*m.n*]paracyclophane family with *m* and *n* up to 4 (with a selection of leading references).

Beginning with row 1 of the matrix, the subgroup of the [0.*n*]phanes, only one derivative, a dicyano[0.0]paracyclophane has been reported in the literature.[6,7] In row 2 [1.1]-paracyclophane (**1**, $m = n = 1$) has been prepared, a highly reactive intermediate that nevertheless could be investigated by UV/Vis and NMR spectra at –20 °C.[8] The higher homologs given in the Table are again unknown.[9] From *m* = 2 on all combinations are known, and many of them have been thoroughly studied from the structural, spectroscopic and chemical viewpoint, especially [2.2]-[4] and [3.3]paracyclophane.[4] For [4.4]paracyclophane[12] considerably less is known, and for those representatives with unequal molecular bridges – [3.2]-,[10] [4.2]-,[10] and [4.3]paracyclophane,[11] respectively – this is even more pronounced. We hence decided to develop efficient routes to these three hydrocarbons as well as several of their derivatives. The corresponding

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routes to these targets are described in this paper. In the following contribution we will discuss the chemical behavior of these compounds, addressing particularly the question of chemo- and regioselectivity in electrophilic substitution of these phanes.

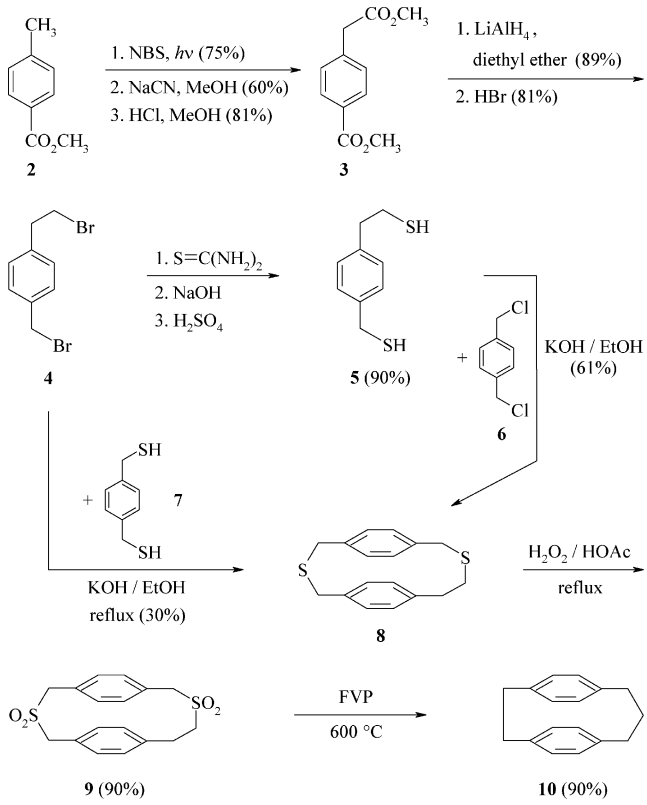
Synthesis of [3.2]- (10), [4.2]- (14) and [4.3]Paracyclophane (19)

For the preparation of the hydrocarbons collected in Scheme 1 essentially three approaches have been developed: cyclizations, ring enlargements and ring contractions. Besides Cram's classical Wurtz cyclizations of appropriate α,ω-dibromides[10,11] more recently Grützmacher has developed a convenient and efficient route based on the McMurry cyclization of 1,3-bis(acylphenyl)propanes (providing for instance the corresponding [3.2]paracyclophenes).[13] To synthesize the appropriate parent systems the respective dialdehydes have to be ring-closed – and in these cases the yield is low. Ring enlargements, usually starting from a [2.2]paracyclophane derivative, have been used widely.[14–17] However, besides the time-consuming preparation of the respective phane precursors, the yields of these processes are often unsatisfactory. Among the ring contraction reactions the sulfone pyrolysis appeared most promising. Not only has this route been applied to the preparation of [3.3]- and [4.4]paracyclophane already,[12,18–21] but its preparative variability (preparation of functionalized derivatives) and often good yield make it particularly attractive.[22] We hence decided to prepare [3.2]- (**10**), [4.2]- (**14**) and [4.3]paracyclophane (**19**) by this route.

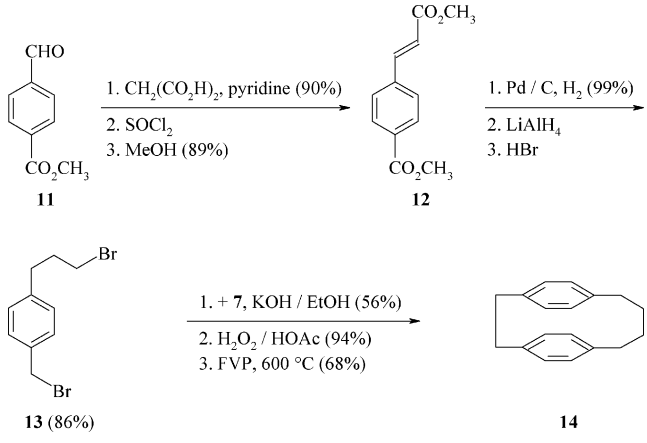
The preparation of **10** is summarized in Scheme 2.

Starting from commercially available methyl 4-methylbenzoate (**2**) this was first converted by NBS bromination, Kolbe nitrile reaction and saponification to the diester **3**, which after LAH-reduction and treatment of the resulting diol with HBr in a sealed ampoule yielded the dibromide **4**. From here on the cyclization to the dithiaphane **8** can either be performed by coupling the dithiol **5**, prepared as shown in Scheme 2, with 1,4-bis(chloromethyl)benzene (**6**) or by reacting **4** directly with the symmetrical dithiol **7**, the yield in the last step of the first route being pronouncedly higher than in the second cyclization. Oxidation of **8** with hydrogen peroxide in acetic acid led to the bis-sulfone **9** which on flash vacuum pyrolysis according to the method of Staab and Haenel[23] and Grütze and Vögtle[24] furnished the hydrocarbon **10** in good overall yield (47% from **5**). All intermediates and the target cyclophane **10** were characterized by their analytical and spectroscopic data (see structure discussion below and Exp. Section), and all compounds are available in gram amounts.

To prepare the next higher homolog, [4.2]paracyclophane (**14**, Scheme 3), methyl 4-formylbenzoate (**11**) was first chain-elongated by a Knoevenagel condensation with malonic acid to the corresponding cinnamic acid. This was esterified via the corresponding acid chloride to **12**, which after catalytic hydrogenation over Pd/C, LAH reduction and bromination gave the dibromide **13**. Both **12**[25] and **13**[26] have been described in the chemical literature before, but the routes presented in Scheme 3 gave far superior yields.



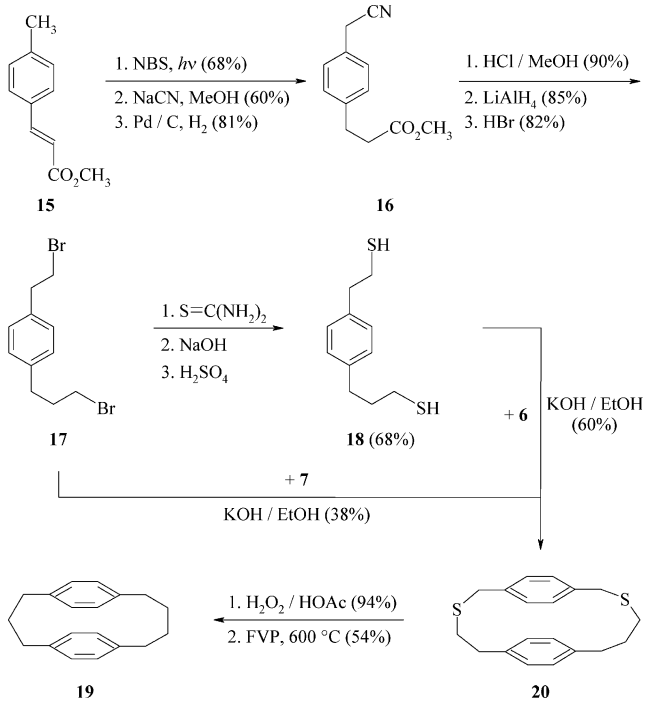
Scheme 2. A preparatively high-yielding route to [3.2]paracyclopane (**10**).



Scheme 3. A preparatively high-yielding route to [4.2]paracyclopane (**14**).

Coupling of **13** with **7** under basic conditions in ethanol yielded the disulfide effortlessly which was oxidized to give the corresponding bis-sulfone with hydrogen peroxide in nearly quantitative yield. Sulfone pyrolysis proceeded in very good yield again (68%) and gave [4.2]paracyclophane (**14**), the structure of which was secured by comparing its spectroscopic data with those of the authentic material.[12]

The last member of this series of unsubstituted hydrocarbons was [4.3]paracyclophane (**19**), synthesized from its constituting aromatic halves as described in Scheme 4.



Scheme 4. Several routes to [4.3]paracyclophane (**19**).

The synthesis started with methyl 4-methylcinnamate (**15**) and followed more or less the same lines as for the preparation of **10** and **14** illustrated in Schemes 2 and 3, respectively. All intermediate compounds were characterized by the usual spectroscopic methods (see Exp. Section), and in the end the phane closure was achieved by either reacting the dibromide **17** with the dithiol **7** or by coupling the dithiol **18** with the dichloride **6**. As above the second alternative gave the dithiaphane – here **20** – in higher yield. Oxidation of **20** with hydrogen peroxide in glacial acetic acid gave the bis-sulfone in excellent yield (94%), and the terminating flash vacuum pyrolysis provided hydrocarbon **19** also in a very satisfying 54% yield. Its spectroscopic data were identical with those of a sample prepared by another route.[11,14]

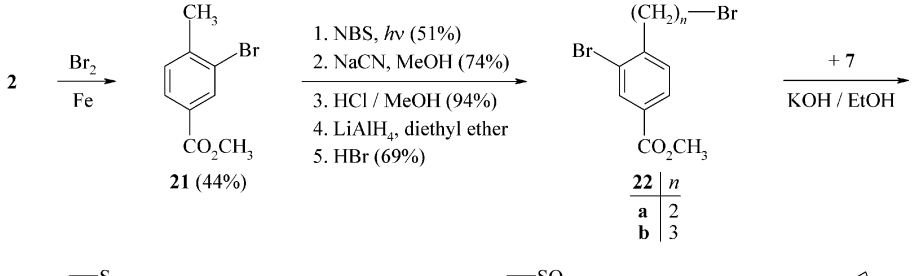
Preparation of Functionalized [3.2]-, [4.2]-, [3.3]-, [4.3]-, and [4.4]Paracyclophanes

For later regioselectivity studies we also prepared a number of functionalized [*m.n*]paracyclophanes. The most important of these are reported in this section; their preparation also demonstrates how different functional groups survive the rather harsh conditions during sulfone pyrolysis.

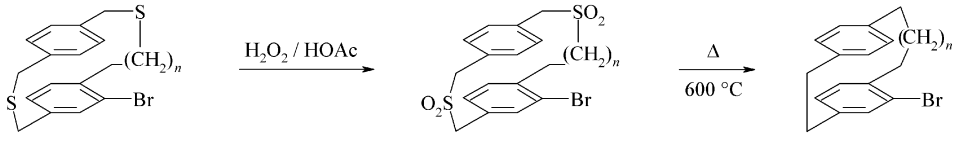
For the preparation of 5-bromo[3.2]paracyclophane (**25a**) and 6-bromo[4.2]paracyclophane (**25b**) the pathways sketched in Scheme 5 were followed.

Beginning with **2** this was first brominated to building block **21** in medium yield. Following the protocols already discussed in the preceding Schemes **21** was converted into the dibromide **22a**. Likewise, using the saturated diester derived from **12** (which had been prepared during the preparation of dibromide **13**; see Scheme 3 and Exp. Section), this was converted into the homologous tribromide **22b** by electrophilic bromination, reduction (LAH), and HBr treatment (for details see Exp. Section). When either **22a** or **b** were coupled with dithiol **7** under basic conditions the two bromothiaphanes **23a/b** resulted in good yield. Hydrogen peroxide oxidation gave the bis-sulfones **24a/b** that split off two equivalents of sulfur dioxide on high-temperature pyrolysis, giving the desired bromo derivatives **25a/b** in satisfactory yield again. The given structure of the two compounds is derived largely from their NMR spectra which are discussed below.

Because of the symmetry of one of the coupling partners, the dithiol **7**, there only results one cyclophane product in the case of **25a** and **b**. This is not the case for methyl [3.3]-paracyclophane-5-carboxylate (**31**) whose precursors were prepared by coupling of methyl 2,5-bis(bromomethyl)benzoate (**26**)[27] with the unsymmetrical dithiol **5**. Now two



22	n
a	2
b	3

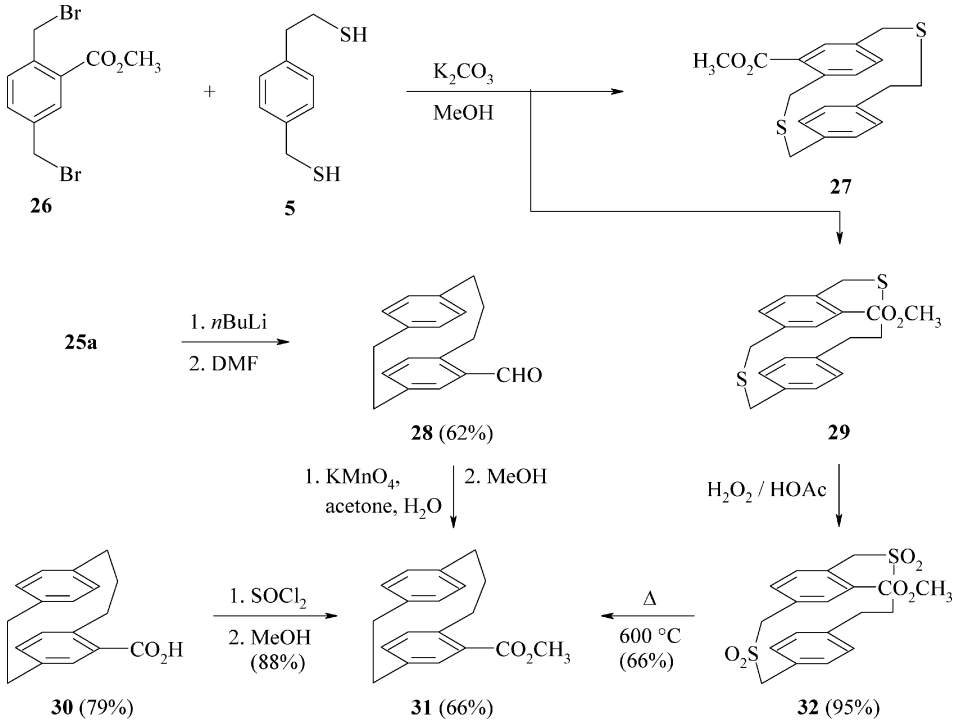


23	n	yield, %
a	1	65
b	2	56

24	n	yield, %
a	1	94
b	2	94

25	n	yield, %
a	1	47
b	2	53

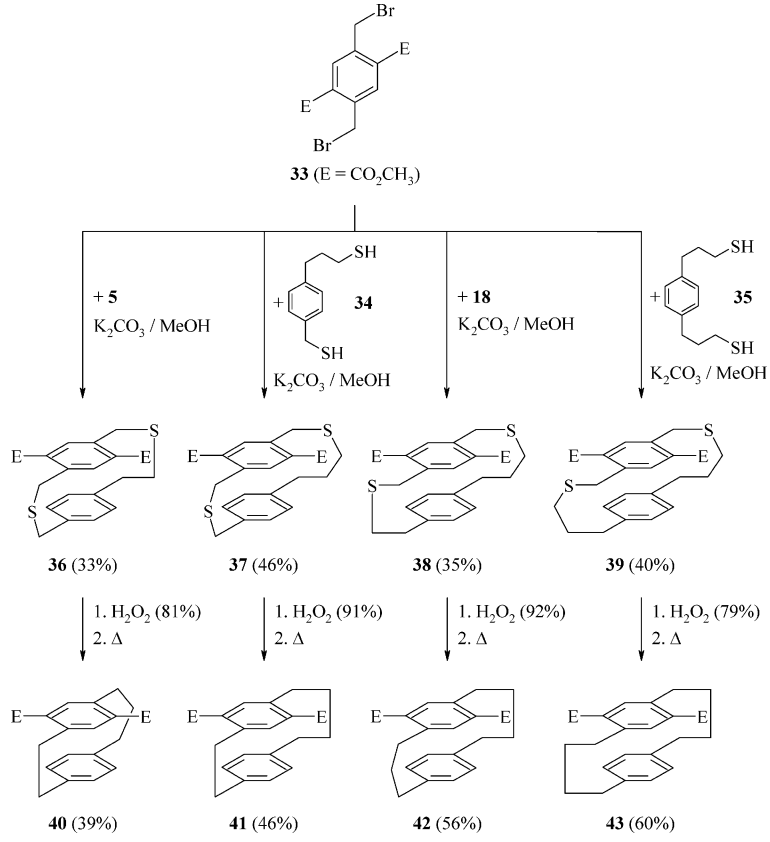
Scheme 5. Synthesis of 5-bromo[3.2]paracyclophane (**25a**) and 6-bromo[4.2]paracyclophane (**25b**).



Scheme 6. Several routes to methyl [3.2]paracyclophane-5-carboxylate (**31**).

coupling products are possible, **27** and **29**, and they were indeed obtained (total yield 54%) in 1:1-ratio (^{1}H NMR analysis, Scheme 6).

Although these regioisomers could not be separated by chromatography, fractional crystallization allowed an enrichment of **29** to 96%. Again the structure assignment of



Scheme 7. The preparation of a selection of [*m.n*]paracyclopane diesters **40**–**43**.

this compound rests largely on its NMR spectra (see below), but in this case an X-ray structural determination of the [3.2]cyclophane derivative **31**[12] resulting from it by sulfone pyrolysis via **32** made the structure proof unambiguous. Furthermore, since **31** could also be connected to **25a** the assignments given for the phane derivatives in Scheme 5 rest on an even more solid basis. The relation between the bromide **25a** and the ester **31** was established as shown in Scheme 6 by converting the former first into the aldehyde **28**, oxidizing it to the acid **30** and esterifying it to **31**, identical in every respect with the sample obtained from **29**.

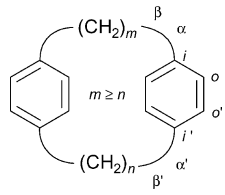
The sulfone pyrolysis also turned out to be the method of choice for the preparation of several [*m.n*]paracyclophane diesters which were needed for the study of transannular effects (see subsequent publication). As shown in Scheme 7 all these transformations started from dimethyl 2,5-bis(bromomethyl)terephthalate (**33**)[28,29] (Scheme 7).

Coupling with the four different dithiols **5**, **34**,[30] **18**, and **35**[21,26] in the presence of potassium carbonate the four dithiaphanes **36**–**39** were obtained, all in acceptable yield. Oxidation to the corresponding bis-sulfones posed no problem and flash vacuum pyrolysis yielded the desired diesters **40**–**43**. The spectroscopic data of the intermediates and the target molecules are collected either in the experimental and/or in the following section, in which ^{1}H and ^{13}C NMR spectroscopic data of key cyclophanes are discussed. The structure determination of **43** (as well as its parent hydrocarbon [4.4]paracyclophane) by single-crystal X-ray structural analysis has already been reported by us earlier.[12]

Structure Determination of Selected [*m.n*]Paracyclophanes by NMR Spectroscopy

Having all the important lower [*m.n*]paracyclophanes at hand we measured their ^{1}H and ^{13}C NMR spectra under comparable conditions and assigned them by two-dimensional techniques (H,C-HSQC and -HMBC) where necessary. The ^{1}H and ^{13}C chemical shifts are given in Table 1. For the compounds with unequal bridges the upper halves of the ^{1}H and the ^{13}C shift blocks refer to the atoms of and adjacent to the longer bridge and the lower halves to the corresponding atoms of the shorter bridge. The data show that problems arise if the spectra are assigned by simple comparison without experimental verification. For example, if one tried to assign the spectra of [3.2]paracyclophane (**10**) by comparing them to those of [2.2]- and [3.3]paracyclophane, one would intuitively assume that the chemical shifts of the three-membered bridge and the adjacent *ipso* (*i*) and *ortho* (*o*) atoms are similar to those of [3.3]paracyclophane and that the two-membered bridge and its vicinity are similarly correlated to [2.2]paracyclophane. Inspection of the experimental findings in Table 1 shows that this is not true. C-*i* in [2.2]paracyclophane is *deshielded* (δ = 139.6 ppm) relative to C-*i* in [3.3]paracyclophane (δ = 138.4 ppm), yet C-*i*′ (adjacent to the two-membered bridge, δ = 137.1 ppm) in [3.2]paracyclophane is *shielded* relative to C-*i* (adjacent to the three-membered bridge, δ = 139.6 ppm) in the same compound.

Table 1. ^{1}H and ^{13}C NMR chemical shifts of some [*m.n*]phane hydrocarbons.[a]



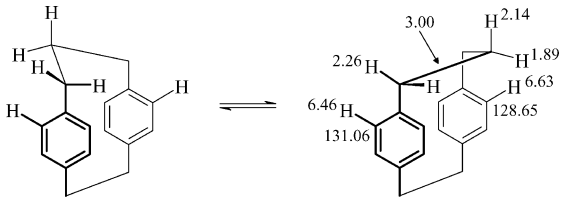
	Paracyclophane					
	[2.2]	[3.2] (**10**)	[4.2] (**14**)	[3.3]	[4.3] (**19**)	[4.4]
^{1}H Chemical shifts						
α-H	3.07	2.69	2.26	2.71	2.26	2.30
β-H	–	2.07	1.42	2.05	1.58	1.56
o-H	6.48	6.56	6.51	6.67	6.52	6.67
α′-H	3.07	2.96	3.00	2.71	2.72	2.30
β′-H	–	–	–	2.05	2.16	1.56
o′-H	6.48	6.37	6.55	6.67	6.67	6.67
^{13}C Chemical shifts						
C-α	35.7	35.5	35.4	36.0	35.7	35.2
C-β	–	32.9	29.0	29.7	29.5	28.9
C-*i*	139.6	139.6	139.7	138.4	138.9	139.3
C-*o*	133.0	130.1	128.1	129.7	128.3	128.4
C-α′	35.7	34.3	34.3	36.0	36.2	35.2
C-β′	–	–	–	29.7	30.3	28.9
C-*i*′	139.6	137.1	137.6	138.4	138.6	139.3
C-*o*′	133.0	132.4	131.1	129.7	129.3	128.4

[a] Solvent $CDCl_3$; references TMS (^{1}H, δ = 0.00 ppm), $CDCl_3$ (^{13}C, δ = 77.0 ppm).

Similar deviations from the "intuitive" assignments are found when one tries to assign the NMR spectra of [4.3]paracyclophane (**19**) by using the data of [3.3]paracyclophane and [4.4]paracyclophane, respectively, as starting points. Here, wrong assignments would be arrived at for the pairs of nuclei C-*i*/*i*′, C-α/α′ and *o*/*o*′-H. Along the same line, we have the finding that the *o*-Hs possess the same chemical shift in [3.3]paracyclophane and [4.4]paracyclophane (δ = 6.67 ppm) whereas in [4.3]paracyclophane (**19**) *o*-H is somewhat shielded (δ = 6.52 ppm) relative to *o*′-H (δ = 6.67 ppm). From the above it is evident that there exists no simple correlation between bridge length and chemical shifts or even order of the chemical shifts. Probably, the different conformational properties of the bridges of different length are responsible for this behavior.

In the ^{1}H NMR spectrum of **10** in CD_2Cl_2 at room temperature the signal of 5-, 9-H appears broader than that of 6-, 8-H and the ^{13}C NMR signal of C-5, -9 is also broadened (Scheme 8). Lowering the temperature leads to decoalescence of the latter signal at 252 ± 3 K and to a chemical shift difference of 2.41 ppm (242.7 Hz) at 183 K with individual shifts of 128.65 and 131.06 ppm. These observations are explained by slow conformational interconversion of the three-membered bridge which consists in the forward-backward flipping of the β-CH_2 group between the two *ortho* positions. From the above parameters the barrier to this flipping process was determined as $\Delta G_c^{\ddagger}$ =

48.2 ± 0.8 kJ·mol^{-1}. The spectra at –90 °C were assigned by the NOE observed between the *syn-ortho* proton (δ = 6.63 ppm) and the equatorial α-proton (δ = 3.00 ppm) of the "half boat" three-membered bridge, from inspection of the H,H-coupling patterns and from selective $^{13}C\{^1H\}$ decoupling. Comparable bridge flipping has been described for [3.3]paracyclophane.[31,32] There, the barrier was reported to be 49.0 ± 2.1 kJ·mol^{-1} at 240 K[31] and 50.2 kJ·mol^{-1} at 258 K.[32] This means that the barrier to flipping of one bridge in [3.3]paracyclophane is not substantially affected by shortening the second bridge from three to two members.



Scheme 8. The conformational equilibrium of **10**. Numbers represent ^1H and ^{13}C (C-*o* only) NMR chemical shifts.

Structures of **25a** and **25b**: In the ^1H NMR spectra of **25a** and **25b** the protons of the ethano bridges have rather narrow chemical shift ranges while those of the propano and butano bridges are spread out considerably with respect to the parent hydrocarbons. This indicates the position of the bromo substituent to be *ortho* to the longer bridge in both cases. Confirmation of the structure of **25b** is provided by exclusion. Complete assignments of the ^1H and ^{13}C NMR spectra of the only other possible *ar*-bromo[4.2]paracyclophane, the 7-bromo isomer, were performed. These spectra are distinctly different from those of **25b** (see the next paper in this series). Hence **25b** can only be the 6-bromo isomer.

Structure of **29**: Two of the three isolated methylene groups show proton shifts (δ = 3.74–3.86, m, 4 H) that are very similar to those of the unsubstituted compound **8** (δ = 3.78 and 3.79 ppm for 11- and 13-H) while the signal of the third isolated CH_2 group has moved strongly downfield (δ = 4.51 ppm for the *syn*-proton 1-H_A) and slightly upfield (δ = 3.04 ppm for the *anti*-proton 1-H_B), respectively, in **29** with respect to **8** (δ = 3.32 for 1-H). Such behavior is characteristic of paracyclophane α-protons situated *ortho* to a carbonyl-containing substituent. Hence the ^1H NMR spectrum shows **29** to be the 16-CO_2Me derivative rather than the 15-isomer, a result that is confirmed by X-ray diffraction.

Conclusions

The sulfone pyrolysis is the method of choice to synthesize [*m.n*]paracyclophanes with alkano bridges from m = 3 and n = 2 all the way to m = n = 4. The parent hydrocarbons are obtained in gram amounts, enough for the investigation of the chemical properties of these bridged hydrocarbons on a broad scale. Furthermore, many functional groups (ketones, esters, acids etc.) survive the harsh conditions of the flash vacuum pyrolysis making this method a preparatively useful one for the preparation of [*m.n*]paracyclophane derivatives as well. The chemical behavior of a selection of the new derivatives is described in the accompanying publication.

Experimental Section

General Remarks: Thin-layer chromatography (TLC): Commercial TLC sheets of type "Polygram Sil G/UV_{254}" by Macherey, Nagel & Co. (Düren). Column chromatography: Kieselgel 60 (70–230 mesh) by Merck (Darmstadt). Melting points: Büchi 530 melting point apparatus, uncorrected values. NMR: With internal tetramethylsilane in the given solvent with the following instruments: Bruker AC-200. ^1H NMR (200.1 MHz), ^{13}C NMR (50.3 MHz). Bruker AM-400. ^1H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz). Internal references: tetramethylsilane (δ_H = 0.00 ppm), $CDCl_3$ (δ_C = 77.05 ppm). Hydrogen atoms labelled with the letter A point towards a substituent in an aromatic ring of a cyclophane, whereas the letter B designates the opposite direction (H_A and H_B, respectively). IR: Nicolet 320 FT-IR; KBr pellets. UV/Vis: Beckman UV 5230 and HP 8452 A Diode Array. EI-MS: Finnigan MAT 8430 (70 eV). The following intermediates were either commercially available or prepared by methods described in the literature: 1,4-bis(chloromethyl)benzene (**6**, Aldrich), 1,4-bis(mercaptomethyl)-benzene (**7**),[18–20] methyl 2,5-bis(bromomethyl)benzoate (**26**),[27] dimethyl 2,5-bis(bromomethyl)terephthalate (**33**),[28,29] 1,4-bis(3′-mercaptopropyl)benzene (**35**).[21,26]

Caution: Many of the halide intermediates are strong lachrimators and should be handled with appropriate care.

Preparation of Building Blocks[33]

A) 4-(2′-Mercaptoethyl)-1-(mercaptomethyl)benzene (5): To methyl 4-methylbenzoate (**2**, 80.0 g, 0.53 mol) in carbon tetrachloride (500 mL) was added NBS (108.0 g, 0.95 mol) and the reaction mixture irradiated with a 500-W lamp until the NBS had vanished. The reaction mixture was filtered while hot and the solvent was removed in vacuo. To the residue was added ethanol (200 mL) and the solution kept in the refrigerator overnight. The precipitated bromide (91.4 g, 75%; m.p. 55–56 °C, lit.[34] m.p. 54–55 °C) was filtered off and used without further purification in the next step. – A solution of sodium cyanide (39.1 g, 0.8 mol) in water (50 mL) was added within 15 min to a refluxing solution of methyl 4-(bromomethyl)benzoate (91.4 g, 0.4 mol) in methanol (200 mL). The reaction mixture was heated to reflux for 1 h and poured onto crushed ice (500 g) after cooling to room temp. The residue formed (m.p. 61–62 °C; lit. m.p.[34] 60–63 °C; 40.6 g, 60%) was removed by filtration and used in the next step after drying on air. – Into a solution of methyl 4-(cyanomethyl)benzoate (40.0 g, 0.23 mol) in methanol (300 mL) was passed gaseous HCl and the mixture refluxed for 2 h. After cooling the reaction mixture was poured into ice water (500 mL) and the formed methyl [4-(methoxycarbonyl)-methyl]benzoate (**3**) thoroughly extracted with dichloromethane. The combined organic layers were dried, the solvent was removed by rotary evaporation and the remaining oil distilled under vacuum: 38.7 g (81%) of 3; b.p. 97–9 °C/0.01 Torr, lit.[35] b.p. 161–165 °C/8 Torr. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 2 H, CH_2), 3.68 (s, 3 H, $CH_2CO_2CH_3$), 3.89 (s, 3 H, ar-CO_2CH_3), 7.36, 8.00 ppm (AA′XX′, 2 H each, ar-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 41.0 (CH_2), 52.1 (2 OCH_3), 129.4, 129.9 (CH, C-2, -3, -5, -6), 129.1 (C_q, C-1), 139.2 (C_q, C-4), 166.8 (C_q, ar-C=O),

171.3 ppm (C_q, CH_2-*C*=O). – For the reduction of **3** a solution of 38.7 g (0.19 mol) in anhydrous diethyl ether (250 mL) was added to a suspension of lithium aluminum hydride (11.3 g, 0.3 mol) in anhydrous diethyl ether (1 L) so slowly to keep the diethyl ether refluxing. After completion of the reaction the mixture was heated at reflux for 1 h, and after cooling to room temp. water (11.3 mL), 15% aqueous sodium hydroxide solution (11.3 mL), and water again (34 mL) were added for hydrolysis. The precipitate formed after 1 h of stirring was removed by filtration and washed several times with diethyl ether. The combined organic fractions were dried ($MgSO_4$), the solvent was removed in vacuo and the remaining oil distilled under vacuum: 25.3 g (89%) 1-(hydroxymethyl)-4-(2-hydroxyethyl)benzene, b.p. 147 °C/0.01 Torr; m.p. ca. 30 °C. IR (KBr): $\tilde{\nu}$ = 3230 (vs), 2940 (s), 2860 (s), 1420 (m), 1050 (vs), 1025 (vs), 1010 (vs), 830 (s), 760 (m), 710 (m) cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ = 2.79 (t, 2 H, ar-CH_2-C), 3.71 (t, 2 H, CH_2CH_2OH), 4.54 (s, 2 H, ar-CH_2-O), 7.15 and 7.25 ppm (AA′BB′, 2 H each, ar-H). ^{13}C NMR (101 MHz, CD_3OD): δ = 41.1 (CH_2, 4-CH_2), 65.4, 66.2 (both CH_2, OCH_2), 129.3, 131.1 (both CH, C-2, -3, -5, -6), 140.4, 141.6 ppm (both C_q, C-1, -4). UV (acetonitrile): λ_{max} (log ε) = 219 (3.06), 198 nm (4.16). MS (EI, 70 eV): *m*/*z* (%) = 152 (100) [M^+], 134 (20), 121 (80), 105 (16), 104 (33), 91 (33), 77 (21). $C_9H_{12}O_2$ (152.19): calcd. C 71.03, H 7.95; found C 71.05, H 7.90.

4-(2′-Bromoethyl)-1-(bromomethyl)benzene (4): To a solution of the above diol (7.40 g, 48.6 mmol) in glacial acetic acid (20 mL) was added HBr in acetic acid (ca. 30%, 30 mL) and the mixture heated to 100 °C in a sealed thick-walled ampoule. After cooling to room temp. the ampoule contents were poured onto a mixture of ice and hydrogen carbonate solution. The precipitate was filtered off, dried and purified by silica gel column chromatography with carbon tetrachloride: 11.0 g (81%) of **4**, colorless needles, m.p. 71–72 °C. IR (KBr): $\tilde{\nu}$ = 2920 (w), 1500 (w), 1440 (m), 1430 (m), 1410 (m), 1310 (m), 1220 (s), 1190 (s), 1120 (m), 840 (s), 630 (vs) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.15 (t, 2 H, C$H_2$$CH_2$Br), and 3.55 (t, 2 H, CH_2CH_2Br), 4.48 (s, 2 H, ar-CH_2-Br), 7.37 ppm (AA′BB′, 4 H, ar-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 32.6, 33.3 (2 CH_2Br), 38.9 (*C*$H_2$$CH_2$Br), 129.1, 129.3 (both CH, C-2, -3, -5, -6), 136.4 (C_q C-1), 139.2 ppm (C_q, C-4). UV (acetonitrile): λ_{max} (log ε) = 235 (4.19), 201 nm (4.45). MS (EI, 70 eV): *m*/*z* (%) = 280 (4) [M^+], 278 (7) [M^+], 276 (4) [M^+], 199 (98), 197 (100), 185 (5), 118 (9), 117 (33), 104 (15). $C_9H_{10}Br_2$ (277.99): calcd. C 38.89, H 3.63, Br 57.49; found C 38.87, H 3.60, Br 56.48.

4-(2′-Mercaptoethyl)-1-(mercaptomethyl)benzene (5): A solution of dibromide **4** (14.5 g, 0.05 mol) and thiourea (8.40 g, 0.11 mol) in ethanol (150 mL) was refluxed for 4 h. On cooling to room temp. the thiuronium salt precipitated which was filtered off and hydrolyzed with sodium hydroxide (10.4 g, 0.26 mol) in water (150 mL) without further purification to the dithiol **5**: 8.65 g (90%), b.p. 97 °C/0.01 Torr. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.38, 1.75 (both t, 1 H each, SH), 2.72–2.79 (m, 2 H, CH_2CH_2-S), 2.88 (t, 2 H, ar-CH_2C), 3.71 (d, 2 H, ar-CH_2S), 7.11–7.27 ppm (AA′BB′, 4 H, ar-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 25.9, 28.5 (2 SCH_2), 39.8 (4-CH_2), 128.1, 128.3 (CH, C-2, -3, -5, -6), 138.6, 139.3 ppm (C_q, C-1, -4). MS (EI, 70 eV): *m*/*z* (%) = 184 (87) [M^+], 151 (100), 137 (42), 117 (31), 115 (7), 105 (10), 104 (37). $C_9H_{12}S_2$ (184.31), calcd. C 58.65, H 6.56, S 34.79; C 58.64, H 6.53, S 35.05.

The preparation of the cyclophanes from the respective building blocks is described below under *General Procedures.*

B) 1-(Bromomethyl)-4-(3′-bromopropyl)benzene (13): To a solution of malonic acid (22.82 g, 0.22 mol) in anhydrous pyridine (100 mL) were added at room temperature methyl 4-formylbenzoate (11, 30.0 g, 0.18 mol) and piperidine (2 mL). The mixture was heated to reflux until the formation of carbon dioxide stopped. After cooling to room temp. the reaction solution was poured onto ice/concd. hydrochloric acid. The acid formed began to precipitate, and to conclude the crystallization process the reaction mixture was kept in the refrigerator for a few h. The acid was filtered off, washed with water several times, dried, and recrystallized from ethanol: 34.04 g (90%) methyl (*E*)-4-(2-carboxyvinyl)benzoate, colorless needles (ethanol), m.p. 246 °C. IR (KBr): $\tilde{\nu}$ = 2953 (w), 2929 (m), 1714 (s), 1683 (m), 1633 (m), 1279 (vs), 992 (w), 992 (w), 943 (w), 855 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.00 (s, 3 H, CH_3), 6.56 (d, *J* = 16.1 Hz, 1 H, α-CH=), 7.87 (d, *J* = 16.1 Hz, 1 H, β-CH=), 7.65 and 8.09 ppm (AA′XX′, 2 H each, ar-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 53.4 (OCH_3), 118.9 (CH, =CH-α), 128.7, 130.6 (CH, C-2, -3, -5, -6), 131.4 (C_q, C-1), 138.4 (C_q, C-4), 147.4 (CH, =CH-β), 168.5 (C_q, *C*O_2CH_3), 172.9 ppm (C_q, CO_2H). UV (acetonitrile): λ_{max} (log ε) = 192 (4.32), 284 nm (4.43). MS (EI, 70 eV): *m*/*z* (%) = 206 (44) [M^+], 175 (100), 147 (26). $C_{11}H_{10}O_4$ (206.20), calcd. 64.08, H 4.89; found 64.09, H 4.86.

Methyl (*E*)-4-[2′-(Methoxycarbonyl)vinyl]benzoate (12): A mixture of the above acid (34.04 g, 0.17 mmol) and thionyl chloride (40 mL) was heated to reflux for 1 h under nitrogen atmosphere. Excess thionyl chloride was distilled off under vacuum and to the remainder methanol (100 mL) was added under ice cooling. The mixture was heated at reflux; small amounts of methanol were added to keep **12** in solution. After cooling to room temp. the diester **12** crystallized out and was removed by filtration. The product obtained was pure enough for the next step: 32.4 g (89%), colorless needles (ethanol), m.p. 125 °C. IR (KBr): $\tilde{\nu}$ = 3016 (w), 2957 (w), 1721 (vs), 1437 (m), 1322 (s), 1282 (s), 1201 (m), 1170 (s), 1108 (s), 983 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.82, 3.92 (2 OCH_3), 6.52 (d, *J* = 16.0 Hz, 1 H, α-CH=), 7.56–7.72 (AA′BB′, 4 H, ar-H), 8.05 ppm (d, *J* = 16.0 Hz, 1 H, β-CH=). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 51.9, 52.3 (2 OCH_3), 120.2 (CH, =CH-α), 127.9, 130.1 (CH, C-2, -3, -5, -6), 131.4 (C_q, C-1), 138.6 (C_q, C-4), 143.4 (CH, =CH-β), 166.4, 166.9 ppm (both C_q, *C*O_2Me). UV (acetonitrile): λ_{max} (log ε) = 192 (4.32), 284 nm (4.43). MS (EI, 70 eV): *m*/*z* (%) = 220 (59) [M^+], 205 (16), 189 (100), 161 (21), 145 (26). $C_{12}H_{12}O_4$ (220.22), calcd. C 65.45, H 5.49; found C 65.44, H 5.54.

Methyl 4-[2-(Methoxycarbonyl)ethyl]benzoate: To a solution of **12** (35.11 g, 0.16 mol) in ethyl acetate (500 mL) was added 1.5 g of Pd/C and the suspension hydrogenated at room temp. until the hydrogen uptake ceased. The solution was passed through a short column filled with sodium sulfate, and the solvent was removed by rotary evaporation. The remaining oil was distilled under vacuum: 35.0 g (99%) of the saturated diester, b.p. 109–110 °C/0.01 Torr. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.65, 3.01 (both t, 2 H each, CH_2CH_2), 3.67 (s, 3 H, $CH_2CO_2CH_3$), 3.90 (s, 3 H, ar-CO_2CH_3), 7.26, 7.96 ppm (AA′XX′, 2 H each, 3-, 5-H and 2-, 6-H, resp.). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 30.9, 35.2 (CH_2CH_2), 51.7, 52.0 (2 OCH_3), 128.4, 129.9 (CH and C_q, C-1, -2, -3, -5, -6), 145.9 (C_q, C-4), 167.0 (C_q, ar-CO_2), 173.0 ppm (C_q, CH_2CO_2). The compound has been described in the lit.[36]

1-(Bromomethyl)-4-(3′-bromopropyl)benzene (13): A solution of the saturated diester (19.07 g, 85.8 mmol) in anhydrous diethyl ether (250 mL) was added dropwise to a suspension of lithium aluminum hydride (7.0 g, 0.18 mol) in diethyl ether (500 mL) at a rate to keep the solvent gently boiling. After the addition was complete, the mixture was heated to reflux for 1 h, and then cooled to room temp. For hydrolysis water (7 mL), sodium hydroxide solution (15% in water, 7 mL), and water again (21 mL) were added and the mixture stirred for 1 h at room temp. The precipitate was filtered off,

washed several times with diethyl ether, and the combined ether phases were dried ($MgSO_4$). After the solvent had been removed in vacuo the raw diol was dissolved in glacial acetic acid (20 mL) and HBr/acetic acid (ca. 30%, 40 mL) was added. The reaction mixture was heated in a thick-walled ampoule for 8 h at 100 °C. The cooled reaction mixture was poured onto an ice water/soda mixture and the formed **13** extracted by washing four times with 50 mL portions of dichloromethane. After work-up of the combined organic layers the residue was distilled under vacuum: 14.05 g (86%) of **13**, b.p. 99–101 °C/0.001 Torr. The spectroscopic properties of the compound agreed with those reported in ref.[26]

c) 1-(2′-Mercaptoethyl)-4-(3′-mercaptopropyl)benzene (18): Methyl 4-methylcinnamate (15, 56.19 g, 0.32 mol) was brominated with NBS as described above. After termination of the process the reaction mixture was filtered while still hot, and the solvent was removed in vacuo. Vacuum distillation afforded 55.60 g (68%) of methyl (*E*)-4-(bromomethyl)cinnamate, m.p. 58–59 °C; b.p. 163 °C/0.1 Torr. IR (KBr): $\tilde{\nu}$ = 3020 (w), 2955 (w), 1725 (vs), 1640 (m), 1600 (m), 1510 (m), 1440 (s), 1320 (vs), 1280 (s), 1230 (s), 1200 (s), 1170 (vs), 985 (s), 930 (m), 835 (s), 785 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, CH_3), 4.49 (s, 2 H, CH_2), 6.44 (d, J = 16.0 Hz, 1 H, α-CH=), 7.39–7.52 (AA′BB′, 4 H, ar-H), 7.67 ppm (d, J = 16.0 Hz, 1 H, β-CH=). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 32.7 (CH_2), 51.8 (CH_3), 118.5 (CH, =CH-α), 128.5, 129.6 (both CH, C-2, -6, C-3, -5), 134.5 (C_q, C-4), 139.9 (C_q, C-1), 143.9 (CH, =CH-β), 167.2 ppm (C_q, CO_2). UV (acetonitrile): λ_{max} (log ε) = 286 (4.47), 223 (sh, 4.08), 218 (4.17), 198 nm (4.17). MS (EI, 70 eV): *m*/*z* (%) = 256 (5) [M^+], 254 (5) [M^+], 225 (3), 223(3), 175 (100), 144 (14), 116 (14), 115 (50). $C_{11}H_{11}BrO_2$ (255.11): calcd. C 51.79, H 4.35, Br 31.32; found C 51.85, H 4.28, Br 31.14.

Methyl (*E*)-4-(Cyanomethyl)cinnamate: As described above under a) (*E*)-4-(bromomethyl)cinnamate (54.0 g, 0.21 mol) was treated with sodium cyanide to provide the corresponding nitrile: 25.47 g (60%), slightly yellow needles (ethanol), m.p. 76–77 °C. IR (KBr): $\tilde{\nu}$ = 3050 (m), 2950 (m), 2250 (m), 1715 (vs), 1675 (m), 1640 (s), 1430 (s), 1420 (m), 1400 (s), 1330 (s), 1315.8 (s), 1305 (s), 1290 (s), 1200 (vs), 1170 (vs), 1115 (m), 1010 (s), 980 (s), 955 (m), 810 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 2 H, CH_2), 3.81 (s, 3 H, CH_3), 6.45 (d, J = 16.0 Hz, 1 H, α-CH=), 7.34–7.55 (AA′BB′, 4 H, ar-H), 7.67 ppm (d, J = 16.0 Hz, 1 H, β-CH=). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 23.5 (CH_2), 51.8 (CH_3), 117.4 (C_q, C≡N), 118.4 (=CH-α), 128.5, 128.7 (both CH, C-2, -6, C-3, -5), 131.9, 134.3 (both C_q, C-1, -4), 143.7 (=CH-β), 167.2 ppm (C_q, CO_2). UV (acetonitrile): λ_{max} (log ε) = 275 (4.38), 223 (sh, 4.08), 218 (4.17), 198 nm (4.17). MS (EI, 70 eV): *m*/*z* (%) = 201 (40) [M^+], 100 (19), 170 (100), 142 (35), 140 (13), 115 (46), 102 (25). $C_{12}H_{11}NO_2$ (201.22): calcd. C 71.63, H 5.51, N 6.96; found C 71.62, H 5.49, N 6.91.

1-(Cyanomethyl)-4-[2′-(methoxycarbonyl)ethyl]benzene (16): To a solution of methyl (*E*)-4-cyanomethylcinnamate (20.29 g, 100.8 mmol) in THF (150 mL) was added 1.0 g Pd/C and the reaction mixture hydrogenated at room temp. until the hydrogen uptake ceased. The solution was filtered through a short column filled with sodium sulfate, the solvent was removed in vacuo, and the remainder was distilled under vacuum: 16.63 g (81%) of **16**, m.p. 42–43 °C; b.p. 134–136 °C/0.001 Torr. IR (KBr): $\tilde{\nu}$ = 3035 (w), 2955 (m), 2253 (w), 1733 (vs), 1515 (m), 1434 (s), 1420 (m), 1373 (m), 1297 (m), 1189 (s), 1179 (s), 1161 (s), 1060 (m), 981 (m), 900 (m), 842 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.62 (t, 2 H, CH_2CO), 2.94 (t, 2 H, ar-CH_2), 3.66 (s, 3 H, OCH_3), 3.70 (s, 2 H, CH_2CN), 7.18–7.28 ppm (AA′BB′, 4 H, ar-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 23.2 (*C*H_2CN), 30.4, 35.5 (CH_2CH_2), 51.6 (OCH_3), 118.0(C_q, C≡N), 127.9 (C_q, C-1), 140.5 (C_q, C-4), 128.1 (CH, C-2, -3, -5, -6), 173.1 ppm (C_q, CO_2). UV (acetonitrile): λ_{max} (log ε) = 211 (3.95), 196 nm (4.23). MS (EI, 70 eV): *m*/*z* (%) = 203 (32) [M^+], 176 (22), 144 (30), 143 (100), 134 (30), 130 (64), 117 (50), 116 (31), 115 (30), 104 (30), 103 (38). $C_{12}H_{13}NO_2$ (203.24): calcd. C 70.92, H 6.45, N 6.89; found C 70.87, H 6.46, N 6.79.

4-[(Methoxycarbonyl)methyl]-1-[2′-(methoxycarbonyl)ethyl]benzene: The same procedure as for the hydrolysis described under a) was employed using 17.43 g (85.8 mmol) of the above nitrile. The raw product was purified by vacuum distillation: 18.29 g (90%) of 4-[(methoxycarbonyl)methyl]-1-[2′-(methoxycarbonyl)ethyl]benzene, m.p. 43–44 °C; b.p. 105–107 °C/0.001 Torr. IR (KBr): $\tilde{\nu}$ = 3032 (m), 2957 (m), 2930 (m), 1735 (vs), 1690 (m), 1514 (s), 1435 (vs), 1370 (s), 1320 (vs), 1303 (vs), 1259 (vs), 1192 (vs), 1145 (vs), 1105 (m), 1007 (s), 979 (s), 900 (m), 875 (m), 797 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.62, 2.93 (both t, 2 H each, CH_2CH_2), 3.59 (s, 2 H, ar-CH_2), 3.66, 3.68 (both s, 3 H each, 2 OCH_3), 7.13–7.22 ppm (AA′BB′, ar-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 30.5 ($CH_2CH_2CO_2$), 35.6 ($CH_2CH_2CO_2$), 40.8 (4-CH_2), 51.6 (2 OCH_3), 128.5, 129.4 (both CH, C-2, -3, -5, -6), 131.9 (C_q, C-4), 139.4 (C_q, C-1), 172.1 (C_q, ar-CH_2CO_2), 173.3 ppm (C_q, $CH_2CH_2CO_2$). UV (acetonitrile): λ_{max} (log ε) = 215 (3.90), 211 (3.93), 196 nm (4.42). MS (EI, 70 eV): *m*/*z* (%) = 236 (48) [M^+], 205 (12), 177 (49), 176 (100), 163 (24), 117 (72). $C_{13}H_{16}O_4$ (236.27): calcd. C 66.09, H 6.83; C 66.11, H 6.85.

1-(2′-Hydroxyethyl)-4-(3′-hydroxypropyl)benzene: As described under a) 4-[(methoxycarbonyl)methyl]-1-[2′-(methoxycarbonyl)ethyl]-benzene (17.03 g) was reduced with lithium aluminum hydride to the corresponding diol; the raw product obtained was distilled under vacuum: 11.01 g (85%) of 1-(2′-hydroxyethyl)-4-(3′-hydroxypropyl)benzene, b.p. 154 °C/0.001 Torr; m.p. 38 °C. IR (KBr): $\tilde{\nu}$ = 3404 (m), 3344 (s), 3248 (m), 2929 (m), 2833 (m), 1515 (m), 1450 (m), 1068 (s), 1053 (vs), 1015 (m), 910 (m), 834 (s), 775 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.84 (m, 2 H, central propyl-CH_2), 2.24 (br. s, 2 H, OH), 2.65, 2.81 (both t, 2 H each, ar-CH_2), 3.62, 3.79 (both t, 2 H each, OCH_2), 7.12 ppm ("s", 4 H, ar-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 31.6 (CH_2, C-1"), 34.2 (CH_2, C-2"), 38.7 (CH_2, C-1′), 62.1 (CH_2, C-3"), 63.6 (CH_2, C-2′), 128.6, 129.0 (d, C-2, -3, -5, -6), 136.0 (C_q, C-1), 139.9 ppm (C_q, C-4). UV (acetonitrile): λ_{max} (log ε) = 218 (3.93), 213 (3.92), 197 nm (4.28). MS (EI, 70 eV): *m*/*z* (%) = 180 (47) [M^+], 150 (32), 149 (45), 132 (33), 131 (100), 118 (18), 117 (32), 105 (33), 104 (43), 91 (35). $C_{11}H_{16}O_2$ (180.25): calcd. C 73.30, H 8.95; found C 73.24, H 8.99.

1-(2′-Bromoethyl)-4-(3′-bromopropyl)benzene (17): As described above the diol (15.0 g, 83.2 mmol) was converted into the corresponding dibromide by HBr treatment. The raw product was purified by vacuum distillation: 20.41 g (82%) of 17, b.p. 127 °C, 0.01 Torr. IR (KBr): $\tilde{\nu}$ = 3014 (m), 2958 (s), 2936 (vs), 2858 (m), 1514 (vs), 1432 (vs), 1266 (vs), 1242 (s), 1209 (s), 1126 (m), 1024 (m), 807 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.14 (m, 2 H, 2"-H), 2.74 (t, 2 H, 1"-H), 3.12 (t, 2 H, 1′-H), 3.37 (t, 2 H, 3"-H), 3.54 (t, 2 H, 2′-H), 7.13 ppm ("s", 4 H, ar-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 33.0, 33.1, 33.6, 34.1 (all CH_2, C-2′, -1", -2", -3"), 39.0 (CH_2, C-1′), 128.7 (CH, C-2, -3, -5, -6); 136.7 (C_q, C-1), 139.1 ppm (C_q, C-4). UV (acetonitrile): λ_{max} (log ε) = 220 (4.05), 213 (4.00), 197 nm (4.45). MS (EI, 70 eV): *m*/*z* (%) = 308 (22) [M^+], 306 (44) [M^+], 304 (22) [M^+], 227 (28), 225 (28), 213 (61), 211 (62), 199 (75), 197 (75), 117 (100). $C_{11}H_{14}Br_2$ (306.04): calcd. C 43.17, H 4.61, Br 52.22; found C 43.84, H 4.68, Br 51.55.

1-(2′-Mercaptoethyl)-4-(3′-mercaptopropyl)benzene (18): As described above the dibromide **17** (10.0 g, 32.7 mmol) was converted into **18**; the raw reaction product was purified by vacuum distil-

lation: 4.75 g (68%) of **18**, b.p. 98–100 °C/0.001 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (m, 2 H, -SH), 1.92–2.88 (m, 10 H, 5 CH_2), 7.11 ppm ("s", 4 H, ar-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 24.0 (CH_2, C-3"), 26.1 (CH_2, C-2′), 33.9, 35.4 (both CH_2, C-1", -2"), 39.8 (CH_2, C-1′), 128.6, 128.7 (both CH, C-2, -3, -5, -6), 137.4 (C_q, C-1), 139.4 ppm (C_q, C-4).

d) 3-Bromo-4-(2′-bromoethyl)-1-(bromomethyl)benzene (22a). – Methyl 3-Bromo-4-methylbenzoate (21): A suspension of iron powder (2.05 g) and a few mL of bromine in carbon tetrachloride (8 mL) were stirred for 1 h before methyl 4-methylbenzoate (**2**, 49.07 g, 0.33 mol) in carbon tetrachloride (75 mL) was added. While the mixture was kept at reflux bromine (16 mL, 0.33 mol) in carbon tetrachloride (12 mL) was added dropwise within 2 h. After refluxing for 14 h the reaction mixture was cooled to room temp., and dichloromethane (200 mL) and sodium hydrogen sulfite (15% in water, 200 mL) were added. The organic layer was separated, and the aqueous carefully extracted with dichloromethane. The combined organic phases were washed with water, sat. hydrogen carbonate solution, and dried (sodium sulfate). After solvent removal in vacuo the remaining oil was distilled under vacuum: 32.74 g (44%) of **21**, b.p. 83–85 °C/0.01 Torr. IR (film): $\tilde{\nu}$ = 2952 (w), 1726 (vs), 1604 (w), 1435 (m), 1294 (vs), 1257 (vs), 1115 (m), 758 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 3.90 (s, 3 H, CH_3O), 7.27 (d, J = 7.9 Hz, 1 H, 5-H), 7.85 (dd, J = 7.9, 1.7 Hz, 1 H, 6-H), 8.18 ppm (d, J = 1.7 Hz, 1 H, 2-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 23.2 (CH_3), 52.2 (CH_3O), 124.8 (C_q, C-3), 128.4 (CH, C-6), 129.5 (C_q, C-1), 130.7 (CH, C-5), 133.4 (CH, C-2), 143.3 (C_q, C-4), 165.8 ppm (C_q, CO_2). UV (acetonitrile): λ_{max} (log ε) = 208 (4.55), 238 nm (4.05). MS (EI, 70 eV): *m*/*z* (%) = 230 (55) [M$^+$], 228 (55), [M$^+$], 199 (100), 197 (100), 171 (18), 169 (18), 149 (6).

Methyl 3-Bromo-4-(bromomethyl)benzoate: As described above for the NBS bromination of **2** (see preparation of **5**), compound **21** (33.61 g, 0.15 mol) was converted into the corresponding benzyl bromide: 22.91 g (51%), m.p. 64–65 °C. IR (KBr): $\tilde{\nu}$ = 3000 (w), 2842 (w), 1715 (vs), 1433 (s), 1393 (vs), 1285 (vs), 1263 (vs), 1227 (s), 1206 (m), 1040 (m), 770 (s), 722 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, CH_3), 4.60 (s, CH_2), 7.53 (d, J = 8.0 Hz, 1 H, 5-H), 7.95 (dd, J = 8.0, 1.6 Hz, 1 H, 6-H), 8.24 ppm (d, J = 1.6 Hz, 1 H, 2-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 32.3 (CH_2), 52.5 (OCH_3), 124.3 (C_q, C-3), 129.0 (CH, C-6), 131.1 (CH, C-6), 131.7 (C_q, C-1), 134.4 (CH, C-2), 141.7 (C_q, C-4), 165.2 ppm (C_q, CO_2). UV (acetonitrile): λ_{max} (log ε) = 210 (4.52), 248 (4.14), 288 nm (3.31). MS (EI, 70 eV): *m*/*z* (%) = 310 (10) [M$^+$], 308 (20) [M$^+$], 306 (10) [M$^+$], 279 (5), 277 (10), 275 (5), 229 (100), 201 (18), 199 (199). $C_9H_8Br_2O_2$ (307.97): calcd. C 35.10, H 2.62, Br 51.89; found C 34.89, H 2.59, Br 53.14.

Methyl 3-Bromo-4-(cyanomethyl)benzoate: As described above (see preparation of **5**) the nitrile was prepared by Kolbe synthesis from the above benzyl bromide: 13.96 g (74%), colorless needles (ethanol), m.p. 52–54 °C. IR (KBr): $\tilde{\nu}$ = 2936 (w), 1724 (vs), 1439 (m), 1410 (m), 1390 (m), 1300 (vs), 1261 (s), 1122 (m), 754 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 2 H, CH_2), 3.94 (s, 3 H, CH_3), 7.63 (d, J = 8.0 Hz, 1 H, 5-H), 8.02 (dd, J = 8.0, 1.7 Hz, 1 H, 6-H), 8.27 ppm (d, J = 1.7 Hz, 1 H, 2-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 25.1 (CH_2), 52.6 (OCH_3), 116.3 (C_q, CN), 123.5 (C_q, C-3), 129.1, 129.6 (both CH, C-5, -6), 131.9 (C_q, C-1), 134.1 (CH, C-2), 134.7 (C_q, C-4), 165.1 ppm (C_q, CO_2). UV (acetonitrile): λ_{max} (log ε) = 206 (4.59), 232 (4.06), 282 nm (3.08). MS (EI, 70 eV): *m*/*z* (%) = 255 (43) [M$^+$], 253 (43) [M$^+$], 224 (100), 222 (100), 196 (21), 194 (21), 115 (36). $C_{10}H_8BrNO_2$ (254.08): calcd. C 47.27, H 3.17, Br 31.45, N 5.51; found C 47.27, H 3.06, Br 31.45, N 5.50.

Methyl 3-Bromo-4-[(methoxycarbonyl)methyl]benzoate: As described above (see preparation of **5**) the above nitrile (13.68 g, 53.8 mmol) was saponified to the corresponding diester: 14.05 g (94%), colorless plates (ethanol), m.p. 97 °C. IR (KBr): $\tilde{\nu}$ = 3012 (w), 2952 (w), 1740 (vs), 1716 (vs), 1438 (s), 1344 (m), 1302 (s), 1290 (vs), 1262 (vs), 1216 (vs), 1197 (m), 1166 (vs), 1117 (m), 968 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.72 (s, 3 H, $CH_2CO_2CH_3$), 3.84 (s, 2 H, CH_2), 3.91 (s, 3 H, ar-CO_2CH_3), 7.36 (d, J = 7.9 Hz, 1 H, 5-H), 7.93 (dd, J = 7.9, 1.7 Hz, 1 H, 6-H), 8.23 ppm (d, J = 1.7 Hz, 1 H, 2-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 41.5 (CH_2), 52.2, 52.4 (2 OCH_3), 128.6 (CH, C-6), 131.4 (C_q, C-5), 133.8 (C_q, C-2), 125.0 (C_q, C-3), 130.8 (C_q, C-1), 139.1 (C_q, C-4), 165.5 ppm (C_q, CO_2). UV (acetonitrile): λ_{max} (log ε) = 192 (4.56), 208 (4.61), 236 (4.10), 282 nm (3.17). MS (EI, 70 eV): *m*/*z* (%) = 288 (2) [M$^+$], 286 (2) [M$^+$], 257 (7), 255 (7), 229 (18), 227 (18), 207 (100). $C_{11}H_{11}BrO_4$ (287.11): calcd. C 46.02, H 3.86, Br 27.83; found C 46.02, H 3.86, Br 27.93.

3-Bromo-4-(2′-bromoethyl)-1-(bromomethyl)benzene (22a): As described above (see preparation of **13**) methyl 3-bromo-4-[(methoxycarbonyl)methyl]benzoate (14.10 g, 49.1 mmol) was reduced with lithium aluminum hydride and the resulting diol treated with HBr/glacial acetic acid: 12.10 g (68%), colorless rhombs (ethanol), m.p. 80–81 °C. IR (KBr): $\tilde{\nu}$ = 3033 (w), 2858 (w), 1485 (w), 1444 (m), 1432 (m), 1220 (vs), 1040 (m), 886 (m), 833 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.28, 3.58 (both t, J = 7.6 Hz, 2 H each, CH_2CH_2), 4.41 (s, 2 H, CH_2), 7.24 (d, J = 7.9 Hz, 1 H, 5-H), 7.30 (dd, J = 7.9, 1.7 Hz, 1 H, 6-H), 7.59 ppm (d, J = 1.7 Hz, 1 H, 2-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 30.8, 31.7 (both CH_2Br), 39.2 (CH_2CH_2Br), 124.3 (C_q, C-3), 128.2 (CH, C-6), 131.4 (CH, C-5), 133.4 (CH, C-2), 138.3, 138.5 ppm (both C_q, C-1, -4). UV (acetonitrile): λ_{max} (log ε) = 208 nm (4.57). MS (EI, 70 eV): *m*/*z* (%) = 360 (2) [M$^+$], 358 (6) [M$^+$], 356 (6) [M$^+$], 354 (2) [M$^+$], 279 (46), 277 (100), 275 (50), 197 (22), 195 (22). $C_9H_9Br_3$ (356.88): calcd. C 30.29, H 2.54, Br 67.14; found C 30.27, H 2.54, Br 67.14.

e) 3-Bromo-4-(3′-bromopropyl)-1-(bromomethyl)benzene (22b). – Methyl 3-Bromo-4-[2′-(methoxycarbonyl)ethyl]benzoate: The saturated diester (20.0 g, 90.0 mmol) prepared from **12** by catalytic hydrogenation (see preparation of **13**) was brominated as described above for **2** (see preparation of **22a**). Silica gel chromatography (carbon tetrachloride) provided 22.91 g (51%) of the bromo derivative, m.p. 66–67 °C. IR (KBr): $\tilde{\nu}$ = 2954 (w), 1736 (s), 1718 (vs), 1430 (m), 1315 (m), 1298 (s), 1258 (s), 1176 (m), 964 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.67 (1′-H), 3.12 (t, 2 H, 2′-H), 3.68 (s, 3 H, $CH_2CO_2CH_3$), 3.91 (s, 3 H, ar-CO_2CH_3), 7.33 (d, J = 8.0 Hz, 1 H, 5-H), 7.89 (dd, J = 8.0, 1.6 Hz, 1 H, 6-H), 8.21 ppm (d, J = 1.6 Hz, 1 H, 2-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 31.5 (CH_2, C-1′), 33.4 (CH_2, C-2′), 51.8, 52.3 (OCH_3), 124.3 (C_q, C-3), 128.6 (CH, C-6), 130.2 (C_q, C-1), 130.3 (CH, C-5), 134.0 (CH, C-2), 144.9 (C_q, C-4), 165.7 (ar-CO_2), 172.7 ppm (CH_2CO_2). UV (acetonitrile): λ_{max} (log ε) = 208 (4.58), 238 nm (4.10). MS (EI, 70 eV): *m*/*z* (%) = 302 (1) [M$^+$], 300 (1) [M$^+$], 271 (6), 269 (6), 221 (100). $C_{12}H_{13}BrO_4$ (301.14): calcd. C 47.86, H 4.35, Br 26.53; found C 47.85, H 4.36, Br 26.60. – To prepare **22b** from this diester, it (7.76 g, 25.8 mmol) was reduced to the corresponding diol with lithium aluminum hydride and this transformed into the tribromide as described above for **22a**; after silica gel chromatography (carbon tetrachloride): 6.33 g (66%), m.p. 72–73 °C. IR (KBr): $\tilde{\nu}$ = 3046 (w), 2955 (w), 1487 (w), 1456 (m), 1288 (m), 1222 (vs), 1040 (m), 888 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.12–2.20 (m, 2 H, 2′-H), 2.89 (t, J = 7.6 Hz, 2 H, 1′-H), 3.42 (t, J = 7.6 Hz, 2 H, 3′-H), 4.41 (s, 2 H, CH_2Br), 7.22 (d, J = 8.0 Hz, 1 H, 5-H), 7.27 (dd, J = 8.0, 1.6 Hz, 1 H, 6-H), 7.58 ppm (d, J = 1.6 Hz, 1 H, 2-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 31.8, 32.3, 32.9, 34.2 (CH_2),

124.4 (C_q, C-3), 128.1 (CH, C-6), 130.8 (CH, C-5), 133.3 (CH, C-2), 137.7 (C_q, C-1), 140.2 ppm (C_q, C-4). UV (acetonitrile): λ_{max} (log ε) = 208 nm (4.55). MS (EI, 70 eV): *m/z* (%) = 374 (4) [M^+], 372 (10) [M^+], 370 (10) [M^+], 368 (4) [M^+], 293 (47), 291 (100), 289 (50), 211 (6), 209 (6), 184 (14), 182 (14). $C_{10}H_{11}Br_3$ (370.91): calcd. C 32.38, H 2.99, Br 64.63; found C 32.45, H 2.88, Br 64.31.

Preparation of Dithia[*m.n*]paracyclophanes

General Procedure: A solution with equimolar amounts of the halide and the dithiol to be coupled in toluene (1 L) was added within 24 h to a vigorously boiling solution of potassium hydroxide (8 equiv.) in a mixture of toluene and ethanol (2 L, ratio 70:30) using a dilution apparatus according to Vögtle.[37] When the addition was complete the mixture was heated for a further 2 h period before it was cooled to room temp. The solvent was removed in vacuo and the remaining solid residue treated wit water (300 mL) and diethyl ether (300 mL). The organic phase was separated, the aqueous extracted with diethyl ether three times. The combined organic layers were dried (sodium sulfate), the solvent was removed and the remainder was purified by silica gel plate chromatography. The following dithia[*m.n*]paracyclophanes were prepared by this route.

a) 2,12-Dithia[4.3]paracyclophane (8): 2.66 g (29%) from **4** (10.80 g, 38.9 mmol) and **7** (6.62 g, 38.9 mmol); 8.14 g (61%) from **5** (8.60 g, 46.7 mmol) and **6** (8.20 g, 46.7 mmol); colorless rhombs (ethanol), m.p. 153 °C. IR (KBr): $\tilde{\nu}$ = 3050 (m), 2950 (m), 2910 (vs), 1510 (s), 1440 (m), 1425 (vs), 1100 (m), 845 (vs), 810 (vs), 770 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.52, 2.84 (both m, 2 H each, 3-, 4-H), 3.32 (s, 2 H, 1-H), 3.78, 3.79 (both s, 2 H each, 11-, 13-H), 6.65–6.87 ppm (m, 8 H, 6-, 7-, 9-, 10-, 15-, 16-, 18-, 19-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 35.6, 35.9 (both CH_2, C-1, -3, -4), 38.3 (CH_2, C-11, -13), 128.0, 128.8, 129.0, 129.1 (CH, C-6, -7, -9, -10, -15, -16, -18, -19), 135.9, 136.8, 137.8, 138.4 ppm (C_q, C-5, -8, - 14, -17). UV (acetonitrile): λ_{max} (log ε) = 197 nm(4.49). MS (EI, 70 eV): *m/z* (%) = 286 (100) [M^+], 150 (7), 149 (36), 136 (67), 118 (16), 117 (28), 104 (54), 91 (94), 89 (21), 77 (51). $C_{17}H_{18}S_2$ (286.46): calcd. C 71.28, H 6.33, S 22.39; found 71.21, H 6.37, S 22.22.

b) 2,13-Dithia[5.3]paracyclophane: 1.67 g (56%) from **7** (1.70 g, 10.0 mmol) and **13** (2.92 g, 10.0 mmol); colorless rhombs (ethanol), m.p. 116 0C. IR (KBr): $\tilde{\nu}$ = 2927 (vs), 2914 (vs), 2851 (m), 1509 (s), 1425 (vs), 1195 (m), 872 (w), 845 (m), 807 (m), 742 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.65–1.75 (m, 2 H, 4-H), 1.96, 2.47 (both t, 2 H each, 3-, 5-H), 3.51 (s, 2 H, 1-H), 3.79 (s, 4 H, 12-, 14-H), 6.69 (d, 2 H), 6.86 (d, 2 H), 6.97 ppm (m, 4 H, 7-, 8-, 10-, 11-, 16-, 17-, 19-, 20-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 25.9, 29.3, 33.8, 34.7 (CH_2, C-1, -3, -4, -5), 38.5, 39.0 (CH_2, C-12, -14), 128.4, 128.5, 128.6, 128.7 (CH, C-7, -8, -10, -11, -16, -17, -19, -20), 134.9, 136.3, 137.5, 138.7 ppm (C_q, C-6, -9, -15, -18). UV (acetonitrile): λ_{max} (log ε) = 192 nm (4.86). MS (EI, 70 eV): *m/z* (%) = 300 (100) [M^+], 196 (14), 195 (14), 164 (24), 163 (57), 162 (30), 149 (20), 117 (30), 105 (39), 104 (35), 91 (38). $C_{18}H_{20}S_2$ (300.48): calcd. C 71.95, H 6.71, S 21.34; found C 71.98, H 6.80, S 21.39.

c) 2,14-Dithia[5.4]paracyclophane (20): 3.86 g (37.5%) from **7** (5.6 g, 32.7 mmol) and **17** (10.0 g, 32.7 mmol); 4.21 g (60%) from **6** (3.9 g, 22.1 mmol) and **18** (4.7 g, 22.1 mmol); colorless needles (ethanol), m.p. 128–129 °C. IR (KBr): $\tilde{\nu}$ = 3048 (w), 3005 (w), 2926 (vs), 2916 (vs), 1510 (s), 1438 (m), 1422 (s), 1098 (m), 823 (m), 771 (w), 703 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.75–1.83, 1.85–1.92, 2.58–2.62, 2.82–2.86 (all m, 2 H each) and 2.55 (t, 2 H, 3-, 4-, 5-, 12-, 13-H), 3.43, 3.56 (both s, 2 H each, 1-, 15-H), 6.78–7.00 ppm (m, 8 H, 7-, 8-, 10-, 11-, 17-, 18-, 20-, 21-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 26.8, 29.1, 33.8, 34.2, 34.4, 34.7 (CH_2, C-1, -3, -4, -5, -12, -13), 37.3 (CH_2, C-15), 128.2, 128.5, 128.7, 128.8 (CH, C-7, -8, -10, -11, -17, -18, -20, -21), 135.6, 137.8, 138.0, 138.2 ppm (C_q, C-6, -9, -16, -19). UV (acetonitrile): λ_{max} (log ε) = 256 (3.38), 197 nm (4.54). MS (EI, 70 eV): *m/z* (%) = 314 (100) [M^+], 281 (10), 247 (812), 210 (40), 209 (36), 164 (24), 163 (47), 149 (24), 131 (22), 117 (41), 105 (51), 104 (50). $C_{19}H_{22}S_2$ (314.50): calcd. C 72.56, H 7.05, S 20.39; found C 72.73, H 7.12, S 2015.

d) 6-Bromo-2,12-dithia[4.3]paracyclophane (23a): 3.98 g (65%) from **7** (2.8 g, 16.7 mmol) and **22a** (6.0 g, 16.7 mmol); colorless needles (ethanol), m.p. 148 °C. IR (KBr): $\tilde{\nu}$ = 2913 (m), 1489 (m), 1416 (vs), 1036 (m), 839 (m), 811 (m), 705 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.19–2.28 and 2.47–2.57 (both m, 1 H each, 3-H), 3.06–3.12 (m, 1 H, 4-H_B), 3.21 (d, *J* = 14.3 Hz, 1 H, 1-H_B), 3.35–3.42 (m, 1 H, 4-H_A), 3.46 (d, 1 H, 1-H_A), 3.68–3.84 (m, 4 H, 11-, 13-H), 6.58–7.08 (m, 6 H, 9-, 10-, 15-, 16-, 18-, 19-H), 7.23 ppm (br. s, 1 H, 7-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 33.2, 36.2, 37.4, 38.1, 38.4 (CH_2, C-1, -3, -4, -11, -13), 123.8 (C_q, C-6), 126.1, 127.5, 128.9, 129.1, 129.7, 131.9, 133.1 (CH, C-7, -9, -10, -15, -16, -18, -19), 136.3, 136.6, 138.4, 138.8 ppm (C_q, C-5, -8, -14, -17). UV (acetonitrile): λ_{max} (log ε) = 194 (4.95), 266 nm (3.75). MS (EI, 70 eV): *m/z* (%) = 366 (4) [M^+], 364 (4) [M^+], 285 (79), 216 (6), 214 (6), 147 (100). $C_{17}H_{17}BrS_2$ (365.36): calcd. C 55.89, H 4.69, Br 21.87, S 17.55; found C 55.49, H 4.63, Br 21.38, S 17.52.

e) 7-Bromo-2,13-dithia[5.3]paracyclophane (23b): 2.39 g (56%) from **7** (2.4 g, 14.3 mmol) and **22b** (5.3 g, 14.3 mmol), colorless needles (ethanol), m.p. 84–85 °C. IR (KBr): $\tilde{\nu}$ = 3019 (w), 2949 (s), 2917 (vs), 2855 (m), 1508 (m), 1440 (s), 1420 (vs), 1042 (m), 872 (s), 826 (m), 766 (m), 738 (s), 701 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.59–1.85, 1.90–2.00 (both m, 2 H each, 3-, 4-H), 2.22–2.31 (m, 1 H, 5-H_B), 2.91–2.99 (m, 1 H, 5-H_A), 3.52, 3.62 (AB, *J* = 14.2 Hz, 1 H each, 1-H), 3.69–3.84 (m, 4 H, 12-, 14-H), 6.65 (d, *J* = 7.8 Hz, 1 H, 11-H), 6.85–6.96 (m, 3 H) and 7.04 ("s", 2 H, 10-, 16-, 17-, 19-, 20-H), 7.26 ppm (d, *J* = 1.7 Hz, 1 H, 8-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 25.5, 27.6, 33.9, 34.2, 38.2, 38.4 (CH_2, C-1, -3, -4, -5, -12, -14), 123.6 (C_q, C-7), 127.2, 128.5, 128.6, 128.8, 130.8, 133.3 (CH, C-8, -10, -11, -16, -17, -19, -20), 134.5, 137.1, 137.6, 138.6 ppm (C_q, C-6, -9, -15, -18). UV (acetonitrile): λ_{max} (log ε) = 196 nm (4.85). MS (EI, 70 eV): *m/z* (%) = 299 (100), 161 (99), 105 (77), 91 (50). $C_{18}H_{19}BrS_2$ (379.37): calcd. C 56.99, H 5.05, S 16.90, Br 21.06; found C 56.99, H 4.99, S 1703, Br 21.06.

f) 16-(Methoxycarbonyl)-2,12-dithia[4.3]paracyclophane (29): 3.7 g (54%) of a mixture of **27** and **29** (ratio 1:1, ^1H NMR analysis) from **5** (3.68 g, 20.0 mmol) and **26** (6.45 g, 20.0 mmol). The mixture was dissolved in warm ethanol, and on cooling to room temperature **29** precipitated (ca. 1.7 g). After 2 additional recrystallizations (ethanol) **29** was obtained as colorless needles in 96% purity; m.p. 136–137 °C. IR (KBr): $\tilde{\nu}$ = 2950 (m), 2920 (m), 1705 (vs), 1440 (m), 1420 (s), 1277 (vs), 1233 (m), 1195 (s), 1077 (s), 845 (m), 800 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.34–2.45 (m, 2 H, 3-H), 2.58–2.65 (m, 1 H, 4-H_B), 3.04 (d, *J* = 14.1 Hz, 1 H, 1-H_B), 3.28–3.35 (m, 1 H, 4-H_A), 3.74–3.86 (m, 4 H, 11-, 13-H), 3.91 (s, 3 H, CH_3), 4.51 (d, *J* = 14.1 Hz, 1 H, 1-H_A), 6.55 (d, *J* = 7.8 Hz, 18-H), 6.66 (dd, *J* = 7.8, 1.8 Hz, 19-H), 6.72–6.77 (m, 2 H), 6.94 (m, 1 H), 6.98 (m, 1 H, 6-, 7-, 9-, 10-, 19-H), 7.61 ppm (d, *J* = 1.8 Hz, 1 H, 15-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 35.9, 36.7, 37.8, 38.2 (CH_2, C-1, -3, -4, -11, -13), 52.0 (OCH3), 128.7, 128.9, 129.3, 130.1, 131.9, 132.4 (CH, C-6, -7, -9, -10, -15, -18, -19); 127.8, 135.8, 137.2, 138.1, 140.8 (C_q, C-5, -8, -14, -16, -17), 167.6 ppm (C_q, CO_2). UV (acetonitrile): λ_{max} (log ε) = 199 nm (4.64). MS (EI, 70 eV): *m/z* (%) = 344 (100) [M^+], 312 (27), 194 (68), 162 (31), 149 (38), 135 (22), 117 (51), 104 (32), 91 (42). $C_{19}H_{20}S_2O_2$ (344.49): calcd. C 66.25, H 5.85, S 18.61; found C 66.25, H 5.89, S 18.36.

Preparation of [*m.n*]Paracyclophane Bis-Sulfones from Their Dithia-precursors

General Procedure: The dithiaphane was treated for extended periods of time (see below) with hydrogen peroxide solution (30%) in the presence of glacial acetic acid (2–3 mL). After the end of the oxidation and cooling to room temp. the residual bis-sulfone was filtered off, washed with diethyl ether and dried under vacuum. The following [*m.n*]paracyclophanes bis-sulfones were prepared by this route.

a) 2,12-Dithia[4.3]paracyclophane 2,2,12,12-Tetraoxide (9): From **8** (2.7 g, 9.43 mmol) in 75 mL hydrogen peroxide solution for 3 d at room temp.: 2.98 g (90%), colorless crystals; m.p. > 250 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2975 (w), 2910 (w), 1515 (w), 1310 (s), 1270 (m), 1140 (w), 1115 (vs), 885 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 350 (3) [M^+], 286 (1), 222 (34), 131 (18), 118 (100), 117 (75), 104 (21). $C_{17}H_{18}S_2O_4$ (350.46): calcd. C 58.26, H 5.18, S 18.30; found C 58.23, H 5.80, S 18.32.

b) 2,13-Dithia[5.3]paracyclophane 2,2,13,13-Tetraoxide: From 2,13-dithia[5.3]paracyclophane (1.45 g, 4.83 mmol) in 75 mL hydrogen peroxide solution for 7 d at room temp: 1.67 g (94%), colorless crystals; m.p. > 250 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2972 (w), 1513 (m), 1318 (vs), 1298 (s), 1272 (vs), 1213 (m), 1116 (vs), 905 (m), 880 (s), 814 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 192 (4.84), 222 nm (3.96). MS (EI, 70 eV): *m*/*z* (%) = 364 (1) [M^+], 300 (3), 274 (3), 236 (46), 208 (24), 104 (100). $C_{18}H_{20}S_2O_4$ (306.04): calcd. C 59.32, H 5.53, S 17.59; found C 59.57, H 5.55, S 17.95.

c) 2,14-Dithia[5.4]paracyclophane 2,2,14,14-Tetraoxide: From 2,14-dithia[5.4]paracyclophane (**20**; 4.13 g, 13.13 mmol) in 100 mL hydrogen peroxide solution for 2 d at reflux: 4.57 g (92%), colorless crystals; m.p. > 250 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3447 (w), 2925 (m), 1512 (m), 1300 (vs), 1259 (m), 1153 (m), 1119 (vs), 903 (m), 829 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 378 (9) [M^+], 314 (76), 313 (65), 295 (10), 251 (229), 250 (100), 248 (17), 222 (39), 207 (12), 145 (18), 131 (37), 118 (90), 117 (83), 104 (66), 91 (17). $C_{19}H_{22}S_2O_4$ (378.50): calcd. C 60.29, H 5.86, S 16.94; found C 60.30, H 5.92, S 16.79.

d) 6-Bromo-2,12-dithia[4.3]paracyclophane 2,2,12,12-Tetraoxide (24a): From **23a** (3.98 g, 5.78 mmol) in 50 mL hydrogen peroxide solution for 12 h at reflux: 3.86 g (84%) of **24a**, colorless crystals, m.p. > 250 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3058 (w), 2926 (w), 1407 (w), 1321 (m), 1272 (m), 1210 (w), 1113 (vs), 887 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 196 (4.89), 228 nm (4.27). MS (EI, 70 eV): *m*/*z* (%) = 430 (5) [M^+], 428 (5) [M^+], 302 (50), 300 (50), 221 (44), 198 (46), 196 (49), 131 (12), 118 (42), 117 (100), 115 (59), 105 (34), 104 (68). HRMS: $C_{17}H_{17}BrS_2O_4$: calcd. 427.9751; found 427.9751.

e) 7-Bromo-2,13-dithia[5.3]paracyclophane 2,2,13,13-Tetraoxide (24b): From **23b** (2.12 g, 5.60 mmol) in 100 mL hydrogen peroxide solution for 24 h at reflux: 2.33 g (94%) of **24b**, colorless crystals, m.p. > 250 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2891 (w), 2923 (w), 1513 (w), 1313 (s), 1273 (s), 1247 (m), 1147 (m), 1113 (vs), 898 (m), 879 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 196 nm (4.87). MS (EI, 70 eV): *m*/*z* (%) = 444 (1) [M^+], 442 (1) [M^+], 316 (20), 314 (20), 288 (5), 286 (5), 235 (14), 184 (25), 182 (25), 104 (100). $C_{18}H_{19}BrS_2O_4$ (306.04): calcd. C 48.76, H 4.32, S 14.46, Br 18.02; found C 48.81, H 4.32, S 14.57, Br 17.96.

f) 16-Methoxycarbonyl-2,12-dithia[4.3]paracyclophane 2,2,12,12-Tetraoxide (32): From **29** (0.90 g, 2.61 mmol) in 50 mL hydrogen peroxide solution for 3 d at room temp.: 1.01 g (95%) of **32**; colorless crystals, m.p. > 250 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3010 (w), 2915 (w), 1703 (s), 1433 (m), 1311 (s), 1282 (s), 1251 (m), 1213 (m), 1112 (vs), 1083 (m), 980 (m), 876 (m), 824 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 198 nm (4.59). MS (EI, 70 eV): *m*/*z* (%) = 408 (1) [M^+], 377 (2), 280 (50), 265 (7), 248 (7), 118 (51), 117 (100).

Flash Vacuum Pyrolysis of [*m.n*]Paracyclophane Bis-Sulfones

General Procedure: The different bis-sulfones were pyrolyzed in small portions (800 to 900 mg) in a pyrolysis apparatus according to Haenel and Staab[23] and Vögtle, respectively.[24] The sulfones were placed in the evaporation zone and the system was evacuated with a diffusion pump while a stream of nitrogen was passed through the apparatus with a capillary; the pressure was estimated to be ca. 0.1 Torr. After the pyrolysis oven had been heated to 600 °C the evaporation oven was heated rapidly to 250 °C and its temperature subsequently increased to 400 °C within 1 h. Behind the pyrolysis zone the pyrolysate was condensed on a cold finger held at –40 °C. The pyrolysates collected from a number of runs were combined and purified either by plate chromatography or MPLC on silica gel.

The following [*m.n*]paracyclophanes were prepared by this route (with only those spectroscopic and analytical data given that are incomplete in the literature).

a) [3.2]Paracyclophane (10): From 2.68 g (7.64 mmol) of **9**: 1.54 g (90%) of **10**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 (br. "qi", 2 H, 2-H), 2.69 (br. "t", 4 H, 1-, 3-H), 2.69 (s, 4 H, 10-, 11-H), 6.37 (*AA′XX′*, 4 H, 6-, 8-, 13-, 17-H), 6.56 ppm (AA′*XX′*, 4 H, 5-, 9-, 14-, 16-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 32.9 (CH_2, C-2), 34.3 (CH_2, C-10, -11), 35.6 (CH_2, C-1, -3), 130.1 (CH, br., C-5, -9, -14, -16), 132.5 (CH, C-6, -8, -13, -17), 137.2 (C_q, C-7, -12), 139.7 ppm (C_q, C-4, -15), assignments by C,H-HETCOR, C,H-COLOC and NOEDIF (10-H → 6-H); for variable-temperature NMR spectra of **10**, see Main Part. MS (EI, 70 eV): *m*/*z* (%) = 222 (55) [M^+], 131 (38), 118 (100), 117 (84), 105 (44), 91 (30).

b) [4.2]Paracyclophane (14): From 1.32 g (3.63 mmol) of 2,13-dithia[5.3]paracyclophane 2,2,13,13-tetraoxide: 586 mg (68%) of **14**; m.p. 73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (narrow m, 4 H, 2-, 3-H), 2.26 (narrow m, 4 H, 1-, 4-H), 3.00 (s, 4 H, 11-, 12-H), 6.54 ppm (AA′BB′, 8 H, ar-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 29.0 (CH_2, C-2, -3), 34.3, 35.4 (CH_2, C-1, -4, -11, -12), 128.1 (CH, C-6, -10, -15, -17), 131.1 (CH, C-7, -9, -14, -18), 137.6 (C_q, C-8, -13), 139.7 ppm (C_q, C-5, -16). MS (EI, 70 eV): *m*/*z* (%) = 236 (100) [M^+], 208 (32), 145 (24), 132 (11), 131 (24), 130 (16), 118 (32), 104 (97).

c) [4.3]Paracyclophane (19): From 3.04 g (8.04 mmol) of **20**: 1.09 g (54%) of **19**; colorless needles, m.p. 116–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (m, 4 H, 2-, 3-H), 2.15 (m, 2 H, 12-H), 2.26 (m, 4 H, 1-, 4-H), 2.71 (m, 4 H, 11-, 13-H), 6.52, 6.68 ppm (AA′XX′, 4 H each, ar-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 29.4 (CH_2, C-2, -3), 30.3 (CH_2, C-12), 35.7, 36.2 (CH_2, C-1, -4, -11, -13), 128.3, 129.2 (CH, C-6, -7, -9, -10, -15, -16, -18, -19), 138.6, 138.8 ppm (C_q, C-5, -8, -14, -17). MS (EI, 70 eV): *m*/*z* (%) = 250 (100) [M^+], 131 (23), 117 (60), 116 (24), 105 (22), 104 (19), 91 (23).

d) 5-Bromo[3.2]paracyclophane (25a): From 3.73 g (8.68 mmol) of **24a**: 1.24 g (47%) of **25a**; colorless needles, m.p. 158–160 °C. IR (KBr): $\tilde{\nu}$ = 2948 (m), 2925 (vs), 2853 (m), 1436 (m), 1040 (m), 898 (m), 826 (s), 808 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85–1.96 (m, 1 H), 2.30–2.41 (m, 1 H), 2.54–3.08 (m, 8 H, 1-, 2-, 3-, 10-, 11-H), 6.29 (m, 2 H), 6.47 (m, 2 H), 6.62 (dd, 1 H), 6.98 (dd, 1 H, 8-, 9-, 13-, 14-, 16-, 17-H), 6.56 ppm (d, *J* = 1.7 Hz, 1 H, 6-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 30.5, 33.7, 34.1, 34.6, 34.9 (CH_2, C-1, -2, -3, -10, -11), 124.7 (C_q, C-5), 127.2, 130.1, 131.6, 131.7, 132.2, 132.6, 136.0 (CH, C-6, -8, -9, -13, -14, -16, -17), 136.7, 138.2, 139.4, 139.7 ppm (C_q, C-4, -7, -12, -15). UV (acetonitrile):

λ_{max} (log ε) = 192 nm (4.80). MS (EI, 70 eV): *m*/*z* (%) = 302 (100) [M^+], 300 (100) [M^+], 222 (10), 221 (52), 131 (20), 118 (65), 117 (99). $C_{17}H_{17}Br$ (301.23): calcd. C 67.79, H 5.69, Br 26.53; found C 67.50, H 5.65, Br 26.72.

e) 6-Bromo[4.2]paracyclophane (25b): From 2.19 g (4.94 mmol) of **24b**: 0.820 g (53%) of **25b**; colorless rhombs, m.p. 155–156 °C. IR (KBr): ṽ = 2940 (vs), 2925 (vs), 2850 (s), 1510 (m), 1440 (s), 1400 (m), 1030 (s), 900 (m), 860 (m), 815 (s), 800 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.05 (br., 1 H), 1.30 (br., 1 H), 1.70 (br. m, 1 H), 1.87 (br. m, 1 H, 2-, 3-H), 1.98 (m, 1 H, 4-H_B), 2.10 (m, 1 H, 1-H_B), 2.45 (m, 1 H, 1-H_A), 2.77–2.93 (m, 3 H, 4-H_A, 11-, 12-H), 3.03–3.17 (m, 2 H, 11-, 12-H), 6.39 (dd, *J* = 7.6, 1.3 Hz, 1 H, 9-H), 6.44 (d, *J* = 7.6 Hz, 10-H), 6.48 (dd, 1 H), 6.61–6.72 (m, 3 H, 14-, 15-, 17-, 18-H), 6.90 ppm (d, *J* = 1.3 Hz, 1 H, 7-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 29.1 (CH_2, C-2, -3), 33.8, 34.1 (CH_2, C-11, -12), 35.1 (CH_2, C-4), 35.5 (CH_2, C-1), 126.9, 128.6, 130.6, 131.5 (CH, C-14, -15, -17, -18), 129.9 (CH, C-10), 130.3 (CH, C-9), 135.0 (CH, C-7), 123.5 (C_q, C-6), 137.1, 138.2, 139.9, 140.0 ppm (C_q, C-5, -8, -13, -16). UV (acetonitrile): λ_{max} (log ε) = 274 (3.06), 198 nm (3.51). MS (EI, 70 eV): *m*/*z* (%) = 316 (49) [M^+], 314 (49) [M^+], 289 (5), 288 (5), 235 (19), 183 (12), 182 (12), 131 (24), 104 (100). $C_{18}H_{19}Br$ (315.25): calcd. C 68.58, H 6.07, Br 25.35; found C 68.52, H 6.03, Br 25.54.

f) Methyl [3.2]Paracyclophane-5-carboxylate (31): From 0.663 g (1.62 mmol) **32**: 0.300 g (66%) **31**, colorless needles, m.p. 83–84 °C. IR (KBr): ṽ = 2950 (m), 2920 (s), 2850 (m), 1700 (vs), 1600 (m), 1450 (s), 1440 (s), 1290 (vs), 1275 (vs), 1240 (m), 1200 (vs), 1180 (s), 1130 (m), 1090 (m), 795 (s), 790 (s), 710 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.04–2.13 (m, 2 H, 2-H), 2.46–2.56 (m, 2 H, 1-H), 2.85 (dt, *J* = 14.0, 5.2 Hz, 1 H, 3-H_B), 2.94–3.02 (m, 4 H, 10-, 11-H), 3.68 (dt, *J* = 14.0, 5.3 Hz, 1 H, 3-H_A), 3.87 (OCH_3), 6.29 (dd, *J* = 7.8, 1.8 Hz, 1 H), 6.41 (dd, *J* = 7.7, 1.9 Hz, 1 H), 6.48 (dd, *J* = 7.6, 1.9 Hz, 1 H), 6.57–6.63 (m, 2 H, 8-, 13-, 14-, 16-, 17-H), 6.56 (d, *J* = 7.7 Hz, 1 H, 9-H), 7.09 ppm (d, *J* = 1.9 Hz, 1 H, 6-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 32.0, 33.9, 34.3, 35.1 (CH_2, C-1, -9, -10, -11), 34.0 (CH_2, br., C-2?), 51.7 (OCH_3), 128.7 (C_q, C-5), 129.5, 130.1, 131.5, 132.7, 133.9 (CH, C-6, -13, -14, -16, -17), 133.4 (CH, br., C-9?), 136.1 (CH, C-8), 136.9, 137.5 (C_q, C-7, -12), 139.7 (C_q, C-15), 142.1 (C_q, C-4), 168.1 ppm (C_q, CO_2). UV (acetonitrile): λ_{max} (log ε) = 203 nm (4.57). MS (EI, 70 eV): *m*/*z* (%) = 280 (100) [M^+], 265 (11), 249 (11), 248 (22), 175 (14), 163 (16), 144 (29), 117 (75), 105 (32). $C_{19}H_{20}O_2$ (280.37): calcd. C 81.40, H 7.19; found C 81.14, H 7.21.

Independent Route to 31: To a solution of **25a** (895 mg, 2.97 mmol) in anhydrous diethyl ether (40 mL) was added at room temp. whilst stirring a solution (5 mL) of *n*BuLi in hexane (15%, 8.0 mmol). After 2 h a solution of DMF (650 mg, 8.9 mmol) in diethyl ether (10 mL) was added, and the mixture was stirred for another 2 h period. For hydrolysis water was added (20 mL), the organic phase was separated and carefully washed with water. After solvent removal in vacuo the residue was purified by MPLC using dichloromethane as the eluent. Besides 190 mg of **10**, 459 mg (62%) of 5-formyl[3.2]paracyclophane (**28**) was isolated, colorless plates (ethanol), m.p. 131 °C. IR (KBr): ṽ = 2952 (m), 2933 (m), 2851 (m), 1688 (vs), 1237 (w), 867 (w), 793 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.02–2.24 (m, 2 H, 2-H), 2.51–2.60 (m, 2 H, 1-H), 2.84–2.91 (m, 1 H, 3-H_B), 2.96–3.09 (m, 4 H, 10-, 11-H), 3. 72 (ddd, *J* = 14.1, 7.2, 3.1 Hz, 1 H, 3-H_A), 6.24 (dd, *J* = 7.9, 1.8 Hz, 1 H), 6.46–6.52 (m, 3 H, 13-, 14-, 16-, 17-H), 6.59 (d, *J* = 7.7 Hz, 1 H, 9-H), 6.63 (dd, *J* = 7.8, 1.9 Hz, 1 H, 8-H), 7.03 (d, *J* = 1.8 Hz, 1 H, 6-H), 10.05 ppm (s, 1 H, CHO). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 32.4 (CH_2, br., C-2?), 32.8, 33.8, 34.0, 34.9 (CH_2, C-1, -3, -10, -11), 129.9, 130.3, 131.5, 132.5, 133.5, 134.9 (CH, C-6, -9, -13, -14, -16, -17), 138.0 (CH, C-8), 133.8, 137.0, 138.5, 139.5, 143.4 (C_q, C-4, -5, -7, -12, -15), 191.7 ppm (CHO). UV (acetonitrile): λ_{max} (log ε) = 192 (4.67), 208 (4.56), 286 nm (3.78). MS (EI, 70 eV): *m*/*z* (%) = 250 (69) [M^+], 146 (26), 145 (17), 118 (27), 117 (100), 115 (25), 105 (42), 91 (26). $C_{18}H_{18}O$ (250.34): calcd. C 86.36, H 7.25; found 86.63, H 7.25.

[3.2]Paracyclophane-5-carboxylic Acid (30): A solution of potassium permanganate (0.5 g, 3.16 mmol) in water (25 mL) was added dropwise to a boiling solution of **28** (0.344 g, 1.37 mmol) in acetone (25 mL).[38] After additional refluxing for 1 h, the solution was cooled to room temp. and the formed manganese dioxide removed by filtration. The aqueous phase was acidified (pH 1), the precipitated acid sucked off and washed several times with water. The raw product was purified by plate chromatography on silica gel (dichloromethane): 0.330 g (78%), colorless needles, m.p. 204 °C. IR (KBr): ṽ = 3064 (w), 3027 (m), 2927 (m), 1684 (vs), 1440 (m), 1306 (m), 932 (w), 913 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.08–2.27 (m, 2 H, 2-H), 2.50–2.60 (m, 2 H) and 2.88–2.95 (m, 1 H, 1-H_A, 1-H_B, 3-H_B), 3.00–3.05 (narrow m, 4 H, 10-, 11-H), 3.84 (ca. ddd, *J* ≈ 14, 7, 3 Hz, 1 H, 3-H_A), 6.32–6.69 (m, 6 H, 8-, 9-, 13-, 14-, 16-, 17-H), 7.29 ppm (d, *J* = 1.9 Hz, 1 H, 6-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 32.2, 33.9, 34.0, 34.6 (br.), 35.1 (CH_2, C-1, -2, -3, -10, -11), 129.7, 130.2, 131.5, 132.8, 133.8 (br.), 134.9, 137.1 (CH, C-6, -8, -9, -13, -14, -16, -17), 127.4 (C_q, C-5), 137.0, 137.8, 139.9, 143.5 (C_q, C-4, -7, -12, -15), 173.0 ppm (C_q, CO_2H). UV (acetonitrile): λ_{max} (log ε) = 200 nm (4.66). MS (EI, 70 eV): *m*/*z* (%) = 266 (42) [M^+], 248 (6), 149 (17), 117 (100), 105 (84). $C_{18}H_{18}O_2$ (266.34): calcd. C 81.17, H 6.81; C 80.61, H 6.94. – Ester **31** from acid **30**: The acid (90 mg, 0.34 mmol) was heated with thionyl chloride (1 mL) for 30 min at reflux. Excess thionyl chloride was distilled off under vacuum and methanol (10 mL) was added to the residue under ice cooling. After boiling to reflux for 30 min, the alcohol was removed in vacuo and the remaining solid purified by MPLC on silica gel with dichloromethane. The spectroscopic data of the isolated ester **31** (84 mg, 88%) were identical with those of the authentic sample described above.

Preparation of the Dithia[*m*.*n*]paracyclophane Diesters 36–39

General Procedure: An equimolar solution of dimethyl 2,5-bis(bromomethyl)terephthalate (**33**)[28,29] and the respective dithiol in THF (500 mL) was added within 12 h to a vigorously boiling solution of potassium carbonate (4 equiv. with respect to the dithiol) in methanol (2 L) using the dilutions apparatus described by Vögtle.[37] When the addition was complete the reaction mixture was boiled for another 2 h before it was cooled to room temp. The solvent was removed completely under vacuum, and to the residue was given water (300 mL) and diethyl ether (300 mL). The organic phase was separated and the aqueous washed three times with 100 mL portions of diethyl ether. The combined organic layers were dried (sodium sulfate), the solvent was removed in vacuo, and the residue purified by plate chromatography on silica gel with dichloromethane.

The following dithia[*m*.*n*]paracyclophane diesters were prepared by this route.

a) Dimethyl 2,12-Dithia[4.3]paracyclophane-15,18-dicarboxylate (36): From **5** (3.97 g, 20.1 mmol) and **33** (7.60 g, 20.1 mmol) 3.90 g (48%) of **36**, colorless needles, m.p. 130–131 °C. IR (KBr): ṽ = 2947 (w), 2918 (w), 1714 (vs), 1432 (m), 1265.8 (s), 1107 (m), 972 (w), 800 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.28–2.42 (m, 2 H, 3-H), 2.62–2.69 (m, 1 H, 4-H_B), 3.07 and 4.45 (AX, *J* = 14.3 Hz, 1 H each, 1-H_B, 1-H_A), 3.67 and 4.69 (AX, *J* = 14.7 Hz, 1 H each, 13-H_B, 13-H_A), 3.33–3.38 (m, 1 H, 4-H_A), 3.71 and 3.86

(AB, J = 15.1, 1 H each, 11-H), 3.94 and 3.95 (2 s, 3 H each, CO_2CH_3), 6.68–6.97 (m, 4 H, 6-, 7-, 9-, 10-H), 7.11 (s, 1 H, 16-H), 7.62 ppm (s, 1 H, 19-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 35.7, 35.9, 36.1 (br.), 36.5, 37.8 (CH_2, C-1, -3, -4, -11, -13), 52.30, 52.32 (2 OCH_3), 128.5, 128.6, 129.0, 129.2, 132.1, 134.5 (CH, C-6, -7, -9, -10, -16, -19), 131.0, 132.0, 135.9, 137.8, 140.5 (C_q, C-5, -8, -14, -15, -17, -18), 167.0, 167.3 ppm (2 CO_2Me). UV (acetonitrile): λ_{max} (log ε) = 194 nm (4.85). MS (EI, 70 eV): m/z (%) = 402 (100) [M^+], 371 (17), 370 (52), 284 (12), 253 (15), 251 (15), 221 (39), 220 (41), 205 (22). $C_{21}H_{22}O_4S_2$ (402.53): calcd. C 62.66, H 5.51, S 15.93; found C 62.67, H 5.55, S 15.90.

b) Dimethyl 2,13-Dithia[5.3]paracyclophane-16,19-dicarboxylate (37): From **34** (3.79 g, 19.1 mmol; prepared from **13** by the thiourea route, see above, preparation of **5**) and **33** (7.23 g, 19.1 mmol) 2.73 g (48%) of **36**, colorless needles, m.p. 104 °C. IR (KBr): $\tilde{\nu}$ = 2949 (w), 2935 (w), 1714 (vs), 1436 (m), 1302 (m), 1263 (s), 1246 (vs), 1135 (m), 1114 (s), 973 (m), 796 cm–1 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66–1.80 (m, 2 H), 1.85–1.98 (m, 1 H), 2.21–2.30 (m, 1 H), 2.43–2.59 (m, 2 H, 3-, 4-, 5-H), 3.24 and 4.47 (AX, J = 14.0 Hz, 1 H each, 1-H_B, 1-H_A), 3.65 and 4.69 (AX, J = 15.1 Hz, 1 H each, 14-H_B, 14-H_A), 3.71 and 3.85 (AB, J = 15.0 Hz, 1 H each, 12-H), 3.93, 3.95 (2 s, 3 H each, OCH_3), 6.67–6.75 (m, 2 H), 6.91–6.98 (m, 2 H, 7-, 8-, 10-, 11-H), 7.34, 7.68 ppm (2 s, 1 H each, 17-, 20-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 26.7, 26.9, 32.3, 33.2, 36.8, 38.6 (CH_2, C-1, -3, -4, -5, -12, -14), 52.31, 52.34 (2 OCH_3), 127.94, 127.89, 128.77, 128.86, 132.8, 133.8 (CH, C-7, -8, -10, -11, -17, -20), 131.3, 131.8, 136.2, 137.7, 137.8, 139.5 (C_q, C-6, -9, -15, -16, -18, -19), 167.1, 167.3 ppm (C_q, 2 CO_2Me). UV (acetonitrile): λ_{max} (log ε) = 192 nm (4.84). MS (EI, 70 eV): m/z (%) = 416 (40) [M^+], 385 (4), 352 (14), 268 (10), 252 (12), 221 (40), 220 (32), 205 (21), 162 (100). $C_{22}H_{24}O_4S_2$ (306.04): calcd. C 63.43, H 5.81, S 15.39; found C 63.49, H 5.82, S 15.63.

c) Dimethyl 2,14-Dithia[5.4]paracyclophane-17,20-dicarboxylate (38): From **18** (3.11 g, 14.7 mmol) and **33** (5.59 g, 14.7 mmol) 2.21 g (39%) of **38**, colorless needles, m.p. 127 °C. IR (KBr): $\tilde{\nu}$ = 3017 (w), 2927 (m), 1720 (vs), 1435 (s), 1312 (m), 1271 (vs), 1233 (s), 1101 (vs), 963 (m), 824 (m), 795 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.75–2.03 (m, 4 H), 2.38–2.61 (m, 4 H), 2.71–2.77 (m, 1 H), 3.21–3.26 (m, 1 H, 3-, 4-, 5-, 12-, 13-H), 3.21 and 4.51 (AX, J = 14.3 Hz, 1 H each), 3.38 and 4.56 (AX, J = 14.1 Hz, 1 H each, 1-, 15-H), 3.91, 3.95 (both s, 3 H each, OCH_3), 6.79 and 6.90 (AA′XX′, 2 H each, 7-, 8-, 10-, 11-H), 7.53, 7.62 ppm (both s, 1 H each, 18-, 21-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 27.6, 28.1, 33.0, 33.2, 34.12, 34.17, 35.5 (CH_2, C-1, -3, -4, -5, -12, -13, -15), 52.32, 52.35 (OCH_3), 128.2 (2 C), 128.5 (2 C), 132.6, 133.7 (CH, C-7, -8, -10, -11, -18, -21), 130.7, 132.1, 137.4, 137.7, 138.1, 140.5 (C_q, C-6, -9, -16, -17, -19, 20), 166.9, 167.0 ppm (C_q, CO_2Me). UV (acetonitrile): λ_{max} (log ε) = 194 (4.83), 244 nm (4.12). MS (EI, 70 eV): m/z (%) = 430 (100) [M^+], 267 (10), 253 (17), 221 (45), 205 (44), 177 (26), 176 (42), 163 (26), 144 (73), 131 (30), 117 (47). $C_{23}H_{26}O_4S_2$ (430.58): calcd. C 64.16, H 6.09, S 14.89; found C 64.18, H 6.06, S 15.14.

d) Dimethyl 2,15-Dithia[5.5]paracyclophane-18,21-dicarboxylate (39): From **35**[21,26] (5.98 g, 26.5 mmol) and **33** (10.03 g, 26.5 mmol) 4.65 g (46%) of **39**, colorless needles, m.p. 107–109 °C. IR (KBr): $\tilde{\nu}$ = 2930 (m), 2854 (w), 1724 (s), 1435 (s), 1268 (vs), 1188 (m), 1102 (vs), 963 (w), 837 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.74–1.97 (m, 8 H, 3-, 4-, 13-, 14-H), 2.53–2.65 (m, 4 H, 5-, 12-H), 3.45 (d, J = 13.8 Hz, 2 H, 1-H_B, 16-H_B), 3.94 (s, 6 H, OCH_3), 4.63 (d, J = 13.8 Hz, 2 H, 1-H_A, 16-H_A), 6.89 (s, 4 H, 7-, 8-, 10-, 11-H), 7.68 ppm (s, 2 H, 19-, 22-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 28.2, 28.9, 33.3, 33.5 (CH_2, C-1, -3, -4, -5, -12, -13, -14, -16), 52.4 (OCH_3), 128.5 (CH, C-7, -8, -10, -11), 133.5 (CH, C-19, -22), 132.1, 137.6, 139.0 (C_q, C-6, -9, -17, -18, -20, -21), 167.1 ppm (C_q, 2 CO_2Me). UV (acetonitrile): λ_{max} (log ε) = 194 (4.84), 242 nm (4.12). MS (EI, 70 eV): m/z (%) = 444 (100) [M^+], 413 (6), 379 (7), 224 (39), 223 (39), 221 (39), 205 (54), 191 (34), 190 (32). $C_{24}H_{28}O_4S_2$ (444.61): calcd. C 64.83, H 6.35, S 14.42; found C 65.04, H 6.62, S 14.70.

Oxidation of the Dithia[*m.n*]paracyclophane Diesters 36–39

Pyrolysis of the Corresponding Bis-Sulfones: The diesters **36–39** were oxidized according to the general procedure described under 4. above, and the resulting bis-sulfones flash vacuum pyrolyzed as reported under 5.

a) Dimethyl [3.2]Paracyclophane-5,8-dicarboxylate (40): Diester **36** (3.20 g, 7.95 mmol) was oxidized with hydrogen peroxide solution (100 mL, reflux for 2 d) to yield 2.97 g (81%) of **15,18-bis(methoxycarbonyl)-2,12-dithia[4.3]paracyclopane 2,2,12,12-tetraoxide**; m.p. (decomp.) > 250 °C. IR (KBr): $\tilde{\nu}$ = 3014 (w), 2914 (w), 1702 (vs), 1433 (m), 1323 (vs), 1302 (vs), 1283 (vs), 1274 (vs), 1252 (vs), 1194 (m), 1113 (vs), 876 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 194 nm (4.86). MS (EI, 70 eV): m/z (%) = 466 (1) [M^+], 435 (5), 402 (6), 388 (100), 323 (17), 306 (22), 219 (14), 118 (17), 117 (28). $C_{21}H_{22}S_2O_8$ (466.53): calcd. C 54.07, H 4.75, S 13.75; found C 54.07, H 4.72, S 13.80. – Pyrolysis of this bis-sulfone (2.55 g, 5.47 mmol) provided **40** (0.72 g, 39%), colorless needles, m.p. 112 °C. IR (KBr): $\tilde{\nu}$ = 2944 (w), 2851 (w), 1712 (vs), 1438 (m), 1271 (vs), 1234 (m), 1185 (m), 1107 (vs), 790 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96–2.13 (m, 2 H, 2-H), 2.49–2.58 (m, 2 H), 2.72–2.84 (m, 2 H), 2.97 (ddd, J = 12.8, 10.3, 6.6 Hz, 1 H), 3.11 (t, J = 11.5 Hz, 1 H), 3.63 (m, 1 H, 1-, 3-, 11-H, 10-H_B), 3.89, 3.90 (both s, 3 H each, OCH_3), 4.01 (ddd, J = 12.8, 10.3, 1.2 Hz, 10-H_A), 6.33–6.61 (m, 4 H, 13-, 14-, 16-, 17-H), 7.09, 7.25 ppm (both s, 1 H each, 6-, 9-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 32.1, 33.1, 33.8 (br.), 34.3, 35.1 (CH_2, C-1, -2, -3, -10, -11), 51.96, 52.03 (OCH_3), 129.5, 129.9, 130.5, 132.3 (CH, C-13, -14, -16, -17), 135.5, 136.9 (CH, C-6, -9), 132.4, 133.0 (C_q, C-5, -8), 137.1, 139.7, 140.1, 141.9 (C_q, C-4, -7, -12, -15), 166.5, 167.5 ppm (C_q, CO_2Me). UV (acetonitrile): λ_{max} (log ε) = 194 nm (4.97). MS (EI, 70 eV): m/z (%) = 338 (100) [M^+], 323 (34), 307 (9), 306 (12), 218 (12), 205 (9), 119 (15), 117 (41), 105 (26). $C_{21}H_{22}O_4$ (338.40): calcd. C 74.54, H 6.55; found C 74.58, H 6.60.

b) Dimethyl [4.2]Paracyclophane-6,9-dicarboxylate (41): Diester **37** (3.23 g, 7.97 mmol) was oxidized with hydrogen peroxide solution (100 mL, room temp. for 3 d) to yield 3.39 g (91%) of **16,19-bis(methoxycarbonyl)-2,13-dithia[5.3]paracyclopane 2,2,13,13-tetraoxide**; m.p. (decomp.) > 250 °C. IR (KBr): $\tilde{\nu}$ = 3004 (w), 2925 (w), 1707 (vs), 1438 (m), 1318 (s), 1269 (s), 1131.8 (s), 967 (m), 878 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 196 (4.84), 212 (4.55), 214 (4.55), 306 nm (3.25). MS (EI, 70 eV): m/z (%) = 480 (1) [M^+], 449 (6), 416 (10), 352 (65), 337 (10), 324 (20), 320 (15), 293 (15), 220 (15), 204 (39), 131 (41), 104 (100). $C_{22}H_{24}S_2O_4$ (480.55): calcd. C 54.99, H 5.03, S 13.34; found C 54.86, H 5.12, S 13.33. – Pyrolysis of this bis sulfone (2.40 g, 4.99 mmol) provided **41** (0.814 g, 46%), colorless needles, m.p. 110–111 °C. IR (KBr): $\tilde{\nu}$ = 2930 (m), 2860 (w), 1715 (vs), 1437 (m), 1259 (vs), 1190 (m), 1098 (vs), 785 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10–1.70 (br. m, 4 H, 2-, 3-H), 2.10–2.40 (m, 3 H), 2.89 (ddd, J = 12.9, 10.0, 7.5 Hz, 1 H), 3.01–3.18 (m, 2 H, 1-, 2-, 3-, 12-H, 4-H_B, 11-H_B), 3.27 (t, J = 11.6 Hz, 1 H, 4-H_A), 3.88, 3.94 (both s, 3 H each, OCH_3), 3.99 (ddd, J = 2.4, 9.6, 13.0 Hz, 1 H, 11-H_A), 6.45–6.52 (m, 2 H), 6.58–6.66 (m, 2 H, 14-, 15-, 17-, 18-H), 7.20, 7.30 ppm (both s, 1 H each, 7-, 10-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 28.9, 29.2 (br.), 32.6 (br.), 33.0, 33.8 (br.), 35.3 (CH_2, C-1, -2, -3, -4, -11, -12), 52.0 (2

OCH_3), 128.1, 128.4, 129.8, 130.7, 133.5, 136.0 (CH, C-7, -10, -14, -15, -17, -18), 131.4, 132.7, 137.6, 140.0, 140.1, 141.7 (C_q, C-5, -6, -8, -9, -13, -16), 167.0, 167.7 ppm (C_q, CO_2Me). UV (acetonitrile): λ_{max} (log ε) = 192 (4.82), 264 nm (3.87). MS (EI, 70 eV): *m/z* (%) = 352 (100) [M^+], 337 (14), 321 (12), 320 (12), 305 (79), 293 (15), 205 (21),131 (21), 119 (25), 105 (35), 104 (35). $C_{22}H_{24}O_4$ (352.43): calcd. C 74.98, H 6.86; found C 75.11, H 6.92.

c) Dimethyl [4.3]Paracyclophane-6,9-dicarboxylate (42): Diester **38** (2.10 g, 4.88 mmol) was oxidized with hydrogen peroxide solution (100 mL, room temp. for 3 d) to yield 2.23 g (92%) of **17,20-bis-(methoxycarbonyl)-2,14-dithia[5.4]paracyclopane 2,2,14,14-tetraoxide**; m.p. (decomp.) > 250 °C. IR (KBr): $\tilde{\nu}$ = 3008 (w), 2954 (w), 1717 (vs), 1435 (m), 1307 (vs), 1285 (vs), 1251 (m), 1149 (m), 1129 (vs), 807 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 194 (4.86), 214 (4.60), 246 nm (4.01). MS (EI, 70 eV): *m/z* (%) = 494 (1) [M^+], 478 (27), 463 (16), 451 (11), 446 (14), 430 (40), 416 (16), 398 (45), 397 (36), 366 (34), 334 (24), 306 (14), 221 (25), 220 (45), 219 (56), 205 (100), 118 (45); 117 (49). HRMS: $C_{23}H_{26}S_2O_8$: calcd. 494.1069; found 494.1069. – Pyrolysis of this bis sulfone (1.97 g, 4.36 mmol) provided **42** (0.828 g, 56%), colorless needles, m.p. 108–109 °C. IR (KBr): $\tilde{\nu}$ = 2927 (w), 2862 (m), 1715 (vs), 1440 (m), 1263 (vs), 1239 (s), 1185 (m), 1095 (vs), 811 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.31 (m, 1 H), 1.40 (m, 1 H), 1.79 (m, 2 H), 1.99–2.12 (m, 2 H), 2.12–2.28 (m, 2 H), 2.38 (m, 1 H), 2.54–2.67 (m, 2 H), 2.82 (m, 1 H, 1-, 2-, 3-, 12-, 13-H, 4-H_B, 11-H_B), 3.38 (m, 1 H, 4-H_A), 3.67 (m, 1 H, 11-H_A), 3.89, 3.91 (both s, 3 H each, OCH_3), 6.51, 6.58, 6.67, 6.71 (all dd, 1 H each, 15-, 16-, 18-, 19-H), 7.14, 7.42 ppm (both s, 1 H each, 7-, 10-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 28.4, 29.3, 29.5, 33.6, 34.0, 35.3, 35.6 (CH_2, C-1, -2, -3, -4, -11, -12, -13), 51.95, 51.97 (OCH_3), 128.0, 128.3, 128.7, 129.4, 133.3, 134.8 (CH, C-7, -10, -15, -16, -18, -19), 131.4, 132.0 (C_q, C-6, -9), 138.5, 138.8, 140.5, 140.7 (C_q, C-5, -8, -14, -17), 167.6, 167.7 ppm (C_q, CO_2Me). UV (acetonitrile): λ_{max} (log ε) = 196 nm (4.79). MS (EI, 70 eV): *m/z* (%) = 366 (100) [M^+], 335 (14), 334 (29), 275 (11), 203 (9), 145 (17), 118 (19), 117 (25). $C_{23}H_{26}O_4$ (366.46): calcd. C 73.38, H 7.15; found 73.17, H 7.09.

d) Dimethyl [4.4]Paracyclophane-6,9-dicarboxylate (43): Diester **39** (4.14 g, 9.31 mmol) was oxidized with hydrogen peroxide solution (100 mL, reflux for 24 h) to yield 3.73 g (79%) of **18,21-bis(methoxycarbonyl)-2,15-dithia[5.5]paracyclopane 2,2,15,15-tetraoxide**; m.p. (decomp.) > 250 °C. IR (KBr): $\tilde{\nu}$ = 3055 (w), 2945 (m), 1711 (vs), 1453 (m), 1410 (m), 1308 (s), 1278 (vs), 1256 (s), 1163 (m), 1120 (vs), 963 (w), 801 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.05–2.15 (m, 6 H), 2.55–2.85 (m, 6 H, 3-, 4-, 5-, 12-, 13-, 14-H), 3.99 (s, 6 H, OCH_3), 4.03 and 5.57 (AX, *J* = 14.0 Hz, 2 H each, 1-, 16-H), 6.88 (s, 4 H, 7-, 8-, 10-, 11-H), 8.09 ppm (s, 2 H, 19-, 22-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 20.9 (CH_2, C-4, -13), 32.8 (CH_2, C-5, -12), 47.7, 56.4 (CH_2, C-1, -3, -14, -16), 53.1 (OCH_3), 128.9 (CH, C-7, -8, -10, -11), 135.1 (CH, C-19, -22), 130.9, 133.3, 137.2 (C_q, C-6, -9, -17, -18, -20, -21), 165.9 ppm (C_q, CO_2Me). UV (acetonitrile): λ_{max} (log ε) = 194 (4.85), 214 (4.62), 244 nm (3.99). MS (EI, 70 eV): *m/z* (%) = 508 (18) [M^+], 476 (14), 444 (12), 412 (10), 221 (19), 220 (35), 219 (35), 205 (100), 189 (20), 131 (38), 104 (43). $C_{24}H_{28}S_2O_8$ (508.61): calcd. C 56.68, H 5.55, S 12.61; found C 56.61, H 5.66, S 12.56. – Pyrolysis of this bis-sulfone (3.59 g, 7.06 mmol) provided **43** (1.62 g, 60%), colorless needles, m.p. 157 °C. IR (KBr): $\tilde{\nu}$ = 2933 (w), 2857 (m), 1718 (vs), 1510 (m), 1452 (s), 1428 (m), 1262 (vs), 1139 (m), 1095 (vs), 835 (m), 805 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25–1.45 (m, 4 H), 1.80–1.94 (m, 4 H, 2-, 3-, 12-, 13-H), 2.01–2.14 (m, 4 H, 1-, 14-H), 2.46–2.53 (m, 2 H, 4-H_B, 11-H_B), 3.39–3.46 (m, 2 H, 4-H_A, 11-H_A), 3.90 (s, 6 H, OCH_3), 6.66 (m, 4 H, 16-, 17-, 19-, 20-H), 7.32 ppm (s, 2 H, 7-, 10-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 27.8, 28.9 (CH_2, C-2, -3, -12, -13), 33.2, 35.1 (CH_2, C-1, -4, -11, -14), 52.0 (OCH_3), 128.1, 128.8, 133.7 (CH, C-7, -10, -16, -17, -19, -20), 131.2 (C_q, C-6, -9), 139.3, 140.9 (C_q, C-5, -8, -15, -18), 167.5 ppm (C_q, CO_2Me). UV (acetonitrile): λ_{max} (log ε) = 194 (4.84), 202 (4.47), 248 nm (3.97). MS (EI, 70 eV): *m/z* (%) = 380 (100) [M^+], 349 (36), 321 (11), 289 (42), 205 (14), 203 (12), 131 (32), 117 (29), 105 (26), 104 (29), 91 (28). $C_{24}H_{28}O_4$ (380.48): calcd. C 75.76, H 7.42; found C 75.54, H 7.44.

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