Electron Donor-Acceptor Compounds, 45[1]

Syntheses of [2.2]-, [3.3]-, and [4.4]Paracyclophanes with 1,2,4,5-Tetracyanobenzene Units as Electron Acceptors

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[2.2]Paracyclophanes **1**–**4** containing tetracyanobenzene (TCNB) units opposite to different electron donor components have been synthesized via the corresponding substituted dithia[3.3]paracyclophanes **8**, **10**, **12**, and **14**. For the pyrolysis of the disulfones **9**, **11**, **13**, and **15** derived therefrom, due to the very low volatility of these compounds, a modification of the conventional pyrolysis method had to be used. – The syntheses of [3.3]paracyclophanes **16**–**18** via the dithia[4.4]paracyclophanes **19**, **21**, and **23** and the corresponding disulfones **20**, **22**, and **24** are described. [4.4]Paracyclophanes **32** and **33** were prepared from the respective dithia[5.5]paracyclophanes **34** and **36** by pyrolysis of the disulfones **35** and **37**. – As cyclisation components for the synthesis of the mentioned dithiaparacyclophanes several new 1,4-bis(mercaptoalkyl)benzenes with electron-donating substituents were prepared as was the TCNB derivative **5**.

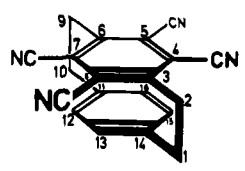
Elektron-Donor-Acceptor-Verbindungen, 45[1]. – Synthesen von [2.2]-, [3.3]- und [4.4]Paracyclophanen mit 1,2,4,5-Tetracyanbenzol-Einheiten als Elektron-Acceptor

Die [2.2]Paracyclophane **1**–**4**, die Tetracyanbenzol(TCNB)-Einheiten gegenüber von verschiedenen Elektron-Donor-Komponenten enthalten, wurden über die entsprechend substituierten Dithia[3.3]paracyclophane **8**, **10**, **12** und **14** synthetisiert. Für die Pyrolyse der davon abgeleiteten Disulfone **9**, **11**, **13** und **15** mußte wegen der sehr niedrigen Flüchtigkeit dieser Verbindungen eine Modifikation der konventionellen Pyrolyse-Methode benutzt werden. – Die Synthesen der [3.3]Paracyclophane **16**–**18** über die Dithia[4.4]paracyclophane **19**, **21** und **23** und die entsprechenden Disulfone **20**, **22** und **24** werden beschrieben. Die [4.4]Paracyclophane **32** und **33** wurden aus den betreffenden Dithia[5.5]paracyclophanen **34** und **36** durch Pyrolyse der Disulfone **35** und **37** dargestellt. – Als Cyclisierungskomponenten für die Synthese der erwähnten Dithiaparacyclophane wurden verschiedene neue 1,4-Bis(mercaptoalkyl)benzole mit Elektron-Donor-Substituenten sowie das TCNB-Derivat **5** dargestellt.

*Inter*molecular electron donor-acceptor complexes with 1,2,4,5-tetracyanobenzene (TCNB) as acceptor component have been studied extensively during the past decades. In this context, *intra*molecular electron donor-acceptor compounds containing TCNB as acceptor unit were of interest because of their well-defined donor-acceptor distances and orientations. The syntheses of [2.2]-, [3.3]-, and [4.4]paracyclophanes with TCNB units facing various electron donors are reported here. In the subsequent paper molecular structures and charge-transfer properties of these compounds are dealt with[2]. Reports on analogous [2.2]metaparacyclophanes[3] and cyclophanes where TCNB units are arranged opposite to naphthalene and anthracene systems[4] will follow.

Synthesis of 4,5,7,8-Tetracyano[2.2]paracyclophanes

General Concept of Synthesis; Precursors: As a general synthesis of the TCNB-[2.2]paracyclophanes **1**–**4** cyclisation of 1,4-bis(bromomethyl)-2,3,5,6-tetracyanobenzene (**5**) with suitably substituted 1,4-bis(mercaptomethyl)benzenes to the corresponding 2,11-dithia[3.3]paracyclophanes was planned from which by sulfur extrusion – either from the dithia[3.3]paracyclophanes themselves by photolysis in trialkyl phosphites, or by photolysis or pyrolysis of the corresponding disulfones – the [2.2]paracyclophanes should be obtained.



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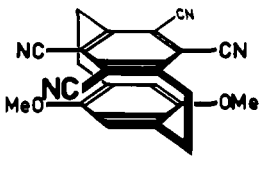

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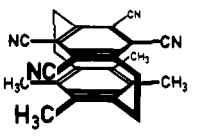

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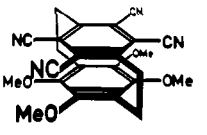

4

Since for the preparation of **5** a direct bromomethylation of 1,2,4,5-tetracyanobenzene was hopeless due to the strong deactivation of the aromatic ring for electrophilic substitution, the side-chain bromination of 1,2,4,5-tetracyano-3,6-dimethylbenzene (**6**) was considered. **6** had been synthesized by a cycloaddition reaction of 3,4-dicyano-2,5-dimethylfuran with dicyanoacetylene and subsequent desoxigenation of the Diels-Alder adduct with triphenylphosphane[5]. We developed a more convenient synthesis of **6** starting from 1,2,4,5-tetrabromo-3,6-dimethylbenzene (**7**) which is easily

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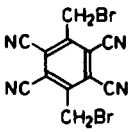
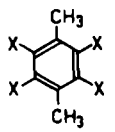
obtained by bromination of *p*-xylene[6]. The substitution of halogeno by cyano groups with copper(I) cyanide in polar aprotic solvents has been applied widely[7]. A problem with *ortho*-dihalogenoarenes is, however, that the *ortho*-dinitriles formed from them frequently react further to the corresponding copper phthalocyanines. Reaction in low concentration in dimethylformamide (DMF)[8] applied to **7** led to **6** in 27% yield[9].



5



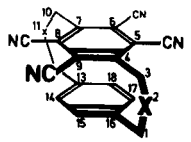
6: X = CN
7: X = Br

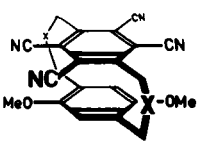
Due to steric and electronic effects the bromination of **6** to **5** was expected to need rather drastic conditions. In fact, the attempt to photobrominate **6** for several hours in boiling trichloromethane or tetrachloroethane left **6** essentially unchanged. Treating **6** with bromine without a solvent (sealed tube, 12 h, 200°C) yielded **5** in a mixture of mono- and unbrominated **6** from which **5** was isolated in only 17% yield; longer reaction times and higher temperatures (220–240°C) led to decomposition. Eventually, photobromination of **6** in 1,2,4-trichlorobenzene (4–5 h, 160°C) yielded **5**, the key cyclisation component for the synthesis of the whole group of TCNB-cyclophanes, in a very satisfying yield (82%).

4,5,7,8-Tetracyano[2.2]paracyclophane (**1**): The cyclisation of **5** with 1,4-bis(mercaptomethyl)benzene to the corresponding dithia[3.3]paracyclophane **8** was performed under high dilution as usually applied for cyclisations to dithiacyclophanes. In this specific case, however, it had to be taken into consideration that due to the four electron-withdrawing substituents the benzylic hydrogens in **5** are so acidic that under basic conditions α- and/or 1,6-eliminations might compete with the cyclisation by nucleophilic substitution; in fact, heating **5** with potassium carbonate in methanol led to a complete decomposition of **5** in a very short time. Therefore, 1,4-bis(mercaptomethyl)benzene was treated with an equivalent amount of potassium hydroxide in methanol, and the solution of the resulting dimercaptide was added synchronously with a solution of **5** in DMF/methanol to a large volume of boiling methanol. For **8**, obtained in 36% yield, analytical data as well as the X-ray structure analysis[2] are in accordance with the structure. With regard to the mentioned acidity of the benzyl groups on TCNB units it is of interest that according to the ^{1}H-NMR spectrum of **8** there is a fast exchange of the benzylic protons on the TCNB side at δ = 4.21 (s, 4H) with deuterium oxide/pyridine whereas the benzylic protons on the unsubstituted paracyclophane side at δ = 4.05 (s, 4H) do not exchange even in the presence of much stronger bases.

The attempted sulfur extrusion from **8** by photolysis in trimethyl phosphite led within 30 min to a complete decomposition of **8** without any formation of **1** (TLC, MS). Therefore, **8** was oxidized with *m*-chloroperbenzoic acid in trichloromethane to the corresponding disulfone **9** (92%, dec. > 260°C). The extreme insolubility and low volatility of **9** complicated the photolysis as well as the pyrolysis. In benzonitrile as a solvent, however, irradiation (150 W Hg high-pressure lamp, duran filter, 100 min) led in 45% yield to **1**. The conventional vapor-phase pyrolysis of sulfones[10] was not applicable to **9** because this disulfone is only scarcely sublimable without decomposition. In a modified pyrolysis procedure a sublimation apparatus with **9** was evacuated to 10^{-3} Torr and was dipped in an air-bath preheated to 520°C. Under these conditions the splitting-off of sulfur dioxide occurred rapidly, and within 3–5 min the formed **1** sublimated from the hot reaction zone to the cooling finger and after chromatography was obtained in 9% yield. Although yields are generally considerably lower than in vapor-phase pyrolysis, the modification described is a useful pyrolysis procedure for poorly volatile sulfones. This method, developed first for the preparation of **1**, was successfully used, for example, in the synthesis of kekulene[11].

1 crystallizes in yellow needles (m.p. 347–350°C, dec.). Elemental analysis, mass spectrum [*m/z* (%) = 308 (24, M^+), 104 (100)] and ^{1}H NMR [δ = 3.37–3.78 (AA'BB', 8H), 6.97 (s, 4H); 80 MHz, $CDCl_3$] agree with the structure proposed for **1** the detailed molecular structure of which has been derived from an X-ray structure analysis[2].





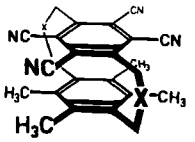
8: X = S
9: X = SO_2

10: X = S
11: X = SO_2

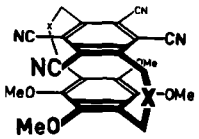
4,5,7,8-Tetracyano-12,15-dimethoxy[2.2]paracyclophane (**2**): Following in general the procedure given above for the synthesis of **8**, by cyclisation of the disodium salt of 1,4-bis-(mercaptomethyl)-2,5-dimethoxybenzene with the TCNB component **5** the correspondingly substituted dithia[3.3]-paracyclophane **10** was obtained (dec. > 330°C; 30%). **10** was oxidized with *m*-chloroperbenzoic acid in trichloromethane to the disulfone **11**. In contrast to the disulfone **9** which yielded **1** photolytically, photolysis of **11** in a benzonitrile suspension did not result in the formation of **2**. The only synthesis of **2** was achieved by applying pyrolysis in the modified version described above. **2** was obtained as deep-violet crystals of m.p. 313–316°C (dec.) in 8% yield from **11**. Elemental analysis, ^{1}H NMR [δ = 2.94–3.76 (m, 8H), 3.84 (s, 6H) 6.26 (s, 2H); 360 MHz, $CDCl_3$] and mass spectra [*m/z* (%) = 368 (23, M^+), 164 (100)] support structure **2**. The molecular structure will be discussed on the basis of an X-ray structure analysis[2].

4,5,7,8-Tetracyano-12,13,15,16-tetramethyl[2.2]paracyclophane (**3**): Cyclisation of **5** with the disodium salt of 1,4-bis(mercaptomethyl)-2,3,5,6-tetramethylbenzene to the correspondingly substituted dithia[3.3]paracyclophane **12** was achieved in analogy to the preparation of **8** and **10**. In spite of the strong sterical crowding due to the complete substitution of both paracyclophane rings, **12** was obtained in

reasonable yield (20.5%). Oxidation of **12** to the disulfone using peroxyacetic acid in acetic acid yielded **13** (83%). Both photolysis of **13** in benzonitrile and pyrolysis of **13** at 500°C/10^{-3} Torr resulted in the formation of **3** (8 and 27% yield, resp.). **3** forms red crystals (dec. > 340°C) for which analysis, ^{1}H NMR [δ = 2.25 (12H), 3.69 (8H); 80 MHz, $CDCl_3$], and mass spectrum [*m/z* (%) = 364 (48, M^+), 160 (100)] confirm the structure.



12: X = S
13: X = SO_2

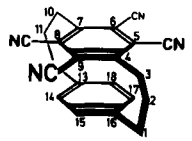


14: X = S
15: X = SO_2

4,5,7,8-Tetracyano-12,13,15,16-tetramethoxy[2.2]paracyclophane (**4**): As the cyclisation component for the donor part in **4**, 1,4-bis(mercaptomethyl)-2,3,5,6-tetramethoxybenzene was prepared from 1,2,4,5-tetramethoxybenzene by chloromethylation to the corresponding bis(chloromethyl) compound (m.p. 126–127°C, 56% yield) which using the thiourea method was converted into the bis(mercaptomethyl) compound (m.p. 118–119°C, 72% yield). Cyclisation with **5** yielded **14** (dec. > 300°C, 14%). Oxidation with peroxyacetic acid led to the disulfone **15** (dec. > 280°C, 90%) from which by pyrolysis at 520°C/10^{-3} Torr **4** was obtained in 19% yield. **4** crystallizes in orange-red prisms (dec. > 350°C) which change colour reversibly to deep red at 120°C. Analysis, ^{1}H NMR [δ = 3.20–3.70 (AA'BB', 8H), 3.84 (12H); 80 MHz, $CDCl_3$] and mass spectrum [*m/z* (%) = 428 (60), 224 (100)] are in accordance with structure **4** for which details will be given based on an X-ray structure analysis[2].

Synthesis of 5,6,8,9-Tetracyano[3.3]paracyclophanes

As models for *inter*molecular interactions [3.3]paracyclophanes are better suited than their [2.2] analogues since in the [3.3]paracyclophane series the aromatic rings are less deformed and the transanular distances are very similar to normal intermolecular distances. 5,6,8,9-Tetracyano[3.3]paracyclophanes which have been synthesized within the scope of the present work include compounds **16**, **17** and **18** the electron donor-acceptor interactions of which will be discussed in comparison with their [2.2]paracyclophane analogues[2].



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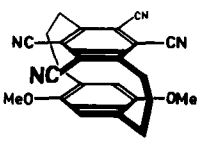

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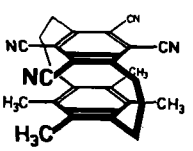
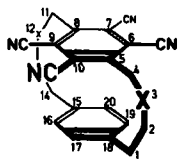


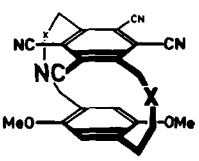
18

The syntheses of these substituted [3.3]paracyclophanes follow the same general concept as those of the [2.2]paracyclophane series: The first step is the cyclisation of **5** with respectively substituted 1,4-bis(mercaptoethyl)benzenes leading to the corresponding 3,12-dithia[4.4]paracyclophanes from which after oxidation to the disulfones by pyrolysis the [3.3]paracyclophanes were to be obtained.

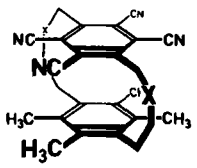
5,6,8,9-Tetracyano[3.3]paracyclophane (**16**): Cyclisation of 1,4-bis(2-mercaptoethyl)benzene, converted with an equivalent amount of sodium hydroxide into the dimercaptide, and **5** by synchronous addition of the two equimolar solutions in high dilution to boiling methanol yielded the dithia[4.4]paracyclophane **19** in 30% yield. By oxidation with *m*-chloroperoxybenzoic acid in trichloromethane the disulfone **20** (dec. > 220°C, 83%) was obtained. Using the pyrolysis technique as described for the synthesis of the corresponding [2.2]paracyclophanes **1**–**4** only traces of the wanted product (<1%) were identified by mass spectrum. Fortunately, the disulfones from the dithia[4.4]paracyclophane series show a slightly higher volatility and can be sublimated without complete decomposition. Therefore, the conventional vapor-phase pyrolysis[10] could be applied to these disulfones. Under conditions given in the Experimental Part **20** was pyrolysed at 580°C/10^{-3} Torr in 11% yield to **16** which was obtained in yellow needles (m.p. 298–302°C). Correct elemental analysis, ^{1}H NMR [δ = 2.25–2.55 (m, 4H), 2.78–3.00 (m, 4H), 3.18–3.35 (m, 4H), 7.10 (s, 4H); 80 MHz, $CDCl_3$] and mass spectrum [*m/z* (%) = 336 (100, M^+)] are in accordance with structure **16**.



19: X = S
20: X = SO_2



21: X = S
22: X = SO_2

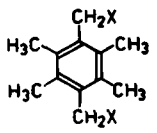


23: X = S
24: X = SO_2

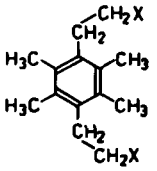
5,6,8,9-Tetracyano-14,17-dimethoxy[3.3]paracyclophane (**17**): Cyclisation of **5** with the disodium salt of 1,4-bis-(2-mercaptoethyl)-2,5-dimethoxybenzene was performed as described for the preparation of **16**. The dithia[4.4]paracyclophane **21** was obtained in 10% yield. After oxidation to the disulfone **22** (*m*-chloroperoxybenzoic acid, trichloromethane/dichloromethane, 62% yield) the pyrolysis to **17** was achieved by the high-vacuum vapor-phase method[10]. **17** was obtained as dark-red prisms (m.p. 332–334°C, dec.;

11% yield). All analytical data including ^{1}H NMR [δ = 2.14–2.28 (m, 2H), 2.44–2.57 (m, 2H), 2.67–2.81 (m, 2H), 3.15–3.29 (m, 6H), 3.89 (s, 6H), 6.56 (s, 2H); 360 MHz, [D_2]dichloromethane] and mass spectrum [*m/z* (%) = 396 (100, M^+)] are in accordance with the structure of **17**. The detailed structure will be discussed on the basis of an X-ray analysis[2].

5,6,8,9-Tetracyano-14,15,17,18-tetramethyl[3.3]paracyclophane (**18**): For the synthesis of **18** the cyclisation component of the donor part of the molecule was prepared in the following way: 1,4-Bis(bromomethyl)-2,3,5,6-tetramethylbenzene (**25**) was treated with sodium cyanide in dimethyl sulfoxide to form the corresponding 1,4-bis(cyanomethyl) compound **26** (m.p. 256–258°C; 94% yield) which was hydrolysed to 2,3,5,6-tetramethyl-1,4-benzenediacetic acid (**27**) and subsequently esterified to the corresponding dimethyl ester **28** (m.p. 116–118°C, 69% yield). $LiAlH_4$ reduction (tetrahydrofuran, 5 h, 20°C) yielded 1,4-bis-(2-hydroxyethyl)-2,3,5,6-tetramethylbenzene (**29**; m.p. 169–170°C; 98%) which was converted to the 1,4-bis(2-bromoethyl) compound **30** (tetrabromomethane, triphenylphosphane, dichloromethane, 88%; m.p. 194–195.5°C). Using the thiourea method (2-methoxyethanol, 3 h reflux) 1,4-bis(2-mercaptoethyl)-2,3,5,6-tetramethylbenzene (**31**; m.p. 149–151°C; 99%) was obtained as the required cyclisation component.



	X
25	Br
26	CN
27	CO_2H
28	CO_2Me

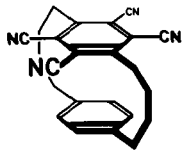


	X
29	OH
30	Br
31	SH

The cyclisation of the disodium salt of **31** with **5** (boiling 2-methoxyethanol, high dilution) resulted in the formation of the dithia[4.4]paracyclophane **23** in 16% yield. The disulfone **24** derived therefrom (*m*-chloroperoxybenzoic acid, dichloromethane, 87%) was pyrolysed in the gas-phase (580°C/10^{-3} Torr) leading to **18** in 18% yield (orange-yellow crystals; m.p. 354°C, dec.). Analytical and spectroscopic data confirm structure **18** [^{1}H NMR (80 MHz, [D_2]dichloromethane): δ = 2.33 (s, 12H), 2.37–2.68 (m, 4H), 3.00–3.43 (8H); MS: *m/z* (%) = 392 (100, M^+)].

Synthesis of 6,7,9,10-Tetracyano[4.4]paracyclophanes

Electron donor-acceptor [4.4]paracyclophanes in comparison with their [3.3]paracyclophane analogues demonstrate the distance dependence of charge-transfer interactions. Whereas [3.3]paracyclophanes have transanular distance between donor and acceptor rings in the order of the sum of the Van der Waals radii (see above), for quinhydrones of the [4.4]paracyclophane type a transanular distance in the order of 390 pm has been determined by X-ray crystallography[12]. In the context of the present investigation the two TCNB-containing [4.4]paracyclophanes **32, 33** have been synthesized.



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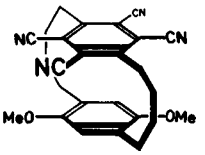
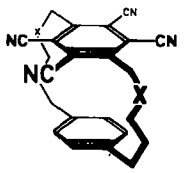
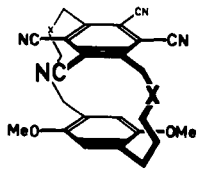


33

6,7,9,10-Tetracyano[4.4]paracyclophane (**32**): For the synthesis of [4.4]paracyclophanes, too, the cyclisation to corresponding dithiaparacyclophanes and the pyrolysis of the disulfones derived therefrom had been used before[12]. Thus, under similar conditions as mentioned above the cyclisation of 1,4-bis(3-mercaptopropyl)benzene[13] and **5** was performed leading to the dithia[5.5]paracyclophane **34** in 33% yield (dec. 234°C). Oxidation (*m*-chloroperoxybenzoic acid, dichloromethane) yielded the disulfone **35** (85%) from which by vapor-phase pyrolysis at 580°C/10^{-3} Torr **32** was obtained. The structure of **32** (colourless crystals, dec. > 360°C) is confirmed by analytical and spectroscopic data including ^{1}H NMR [δ = 1.70–2.20 (m, 8H), 2.30–2.58 (m, 4H), 2.85–3.16 (m, 4H), 6.90 (s, 4H); 80 MHz, [D_2]dichloromethane] and mass spectrum [*m/z* (%) = 364 (100, M^+)].



34: X = S
35: X = SO_2



36: X = S
37: X = SO_2

6,7,9,10-Tetracyano-16,19-dimethoxy[4.4]paracyclophane (**33**): Starting from 1,4-bis(3-bromopropyl)-2,5-dimethoxybenzene[14] using the thiourea method 1,4-bis(3-mercaptopropyl)-2,5-dimethoxybenzene (m.p. 59–60°C, 90% yield) was obtained which was cyclized with **5** to yield the dithia[5.5]paracyclophane **36** (m.p. 238°C, 20.5% yield). Oxidation to disulfone **37** (93%) and vapor-phase pyrolysis of **37** (560°C/10^{-3} Torr, 21% yield) resulted in the formation of **33** (orange-red crystals, dec. > 330°C). Elemental analysis and spectroscopic data like ^{1}H NMR [δ = 1.74–3.08 (m, 16H), 3.79 (s, 6H), 6.39 (s, 2H); 360 MHz, [D_2]dichloromethane] and mass spectrum [*m/z* (%) = 424 (100, M^+)] are in accordance with the suggested structure.

Experimental

1,2,4,5-Tetracyano-3,6-dimethylbenzene (**6**): 84.4 g (0.20 mol) of 1,2,4,5-Tetrabromo-3,6-dimethylbenzene (**7**)[6] and 110 g (1.22 mol) of copper(I) cyanide were heated in 1500 ml of dimethylformamide

(DMF) 5 h under reflux. After cooling to 20°C the reaction mixture was poured into an ice-cold solution of 400 g of iron trichloride hexahydrate in 3 l of 5% hydrochloric acid. The precipitate was filtered off, washed with sodium hydrogen carbonate solution and with water and dried in vacuo. By sublimation (150 to 280°C/0.01 Torr) 16 g of a mixture of **6** and 1,2,4-tricyano-3,6-dimethylbenzene (see below) was obtained which was extracted with trichloromethane. The insoluble material was filtered off and crystallized from acetonitrile: 11 g (27%) of **6**, colourless needles, m.p. 335°C (dec.), identical with **6** prepared according to reference[5]. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.86 (s). – MS: *m/z* (%) = 206 (100, M^+).

From the trichloromethane solution by chromatography on silica from trichloromethane and crystallization from methanol 2.5 g (14%) of colourless prisms (m.p. 153–154°C) was obtained which according to the following data was 1,2,4-tricyano-3,6-dimethylbenzene. The formation of this product is not clear; the simple explanation that there has been incomplete bromination in the preceding stage seems very unlikely according to all analytical data of **7**. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.63 (s, 3H), 2.79 (s, 3H), 7.78 (s, 1H). – MS: *m/z* (%) = 181 (100, M^+).

$C_{11}H_7N_3$ (181.2) Calcd. C 72.91 H 3.89 N 23.19
Found C 72.69 H 4.12 N 22.96

1,4-Bis(bromomethyl)-2,3,5,6-tetracyanobenzene (**5**)

a) 200 mg (0.97 mmol) of thoroughly pulverized **6** and 1 ml of bromine were heated in a sealed tube for 12 h to 200°C. Chromatography on silica from trichloromethane and recrystallization from chlorobenzene resulted in 60 mg (17%) of **5**, colourless crystals, m.p. 261–263°C (dec.). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 4.80 (s). – MS: *m/z* (%) = 362 (5, M^+, 2 Br), 283 (76, Br), 204 (100) a.o.

$C_{12}H_4Br_2N_4$ (364.0) Calcd. C 39.59 H 1.10 Br 43.90 N 15.39
Found C 39.79 H 1.39 Br 43.78 N 15.27

b) To a suspension of 6.0 g (29.1 mmol) of **6** in 180 ml of freshly distilled 1,2,4-trichlorobenzene 1 ml of bromine was added, and the mixture was heated to 160°C by a 300 W daylight-lamp (Osram Vitalux). Further 3 to 4 ml of bromine was added in intervals of 30 to 45 min in portions of 0.5 ml each. The reaction process was followed by ^{1}H NMR: in intervals of 20 to 30 min samples of 0.5 ml were taken and cooled to 20°C; the precipitate was separated and dissolved in [D_6]dimethyl sulfoxide: as soon as the CH_2/CH_3 ratio reached about 10:1, the reaction was stopped to avoid further bromination to the benzal bromide stage. The reaction mixture then was cooled to 20°C, the crystalline raw product was filtered off and washed with tetrachloromethane. By exchange with chlorine (obviously from the solvent) a minor part of the halogenomethyl groups were present as chloromethyl groups which were converted to bromomethyl by treatment with 10 g of pulverized sodium bromide in 30 ml of DMF at 60°C for 30 min. This solution was then diluted with 200 ml ice/water; the precipitate was filtered off, washed with water, dried, and crystallized from chlorobenzene: 8.7 g (82%) of **5**, identical with the product obtained according to procedure a).

5,6,8,9-Tetracyano-2,11-dithia[3.3]paracyclophane (**8**): In a dilution apparatus, equipped with electronically controlled valves regulating dropping rate and dropping volume, solutions of 3.64 g (10 mmol) of **5** in 250 ml of methanol/DMF (10:1) and of 1.70 g (10 mmol) of 1,4-bis(mercaptomethyl)benzene[15] and 20 ml 1 N methanolic KOH in 230 ml of methanol were dropped under nitrogen during 8 h to 1.8 l of boiling methanol. The solution was evaporated in vacuo to a volume of 200 ml and added to 400 ml of water. The precipitate was filtered off, washed with water, dried in vacuo, and chromatographed on silica from dichloromethane. Crystallization from chlorobenzene/ethanol yielded 1.35 g (36%) of **8**, yellow needles, dec. > 320°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 4.05 (s, 4H), 4.21 (s, 4H), 7.30 (s, 4H). – MS: *m/z* (%) = 372 (48, M^+), 135 (100), 103 (24).

$C_{20}H_{12}N_4S_2$ (372.5) Calcd. C 64.50 H 3.25 N 15.04 S 17.22
Found C 64.60 H 3.50 N 14.85 S 17.15

5,6,8,9-Tetracyano-2,11-dithia[3.3]paracyclophane 2,2,11,11-Tetraoxide (**9**): 0.80 g (2.15 mmol) of **8** and 1.72 g (10 mmol) of *m*-chloroperbenzoic acid in 300 ml of trichloromethane were stirred at 20°C for 24 h. The precipitate was washed with methanol and dried in vacuo: 0.86 g (92%) of **9** as yellow crystal powder (dec. > 260°C), practically insoluble in all conventional solvents. The product was therefore used for the following reactions without further purification.

$C_{20}H_{12}N_4O_4S_2$ (436.5) Calcd. C 55.04 H 2.77 N 12.84 S 14.69
Found C 55.52 H 2.73 N 12.46 S 14.43

4,5,7,8-Tetracyano[2.2]paracyclophane (**1**)

a) *By Photolysis of* **9**: A suspension of 1.10 g (2.52 mmol) of **9** in 300 ml of benzonitrile was irradiated under argon (150 W mercury high-pressure lamp, durane filter) until a clear solution was obtained (ca. 100 min). After distilling off the solvent in vacuo the residue was chromatographed from dichloromethane on silica and crystallized from acetonitrile/ethanol: 350 mg (45%) of **1**, yellow needles, m.p. 347–350°C (dec.). – ^{1}H NMR, MS: see Theoretical Part; X-ray structure analysis: see ref.[2].

$C_{20}H_{12}N_4$ (308.3) Calcd. C 77.91 H 3.92 N 18.17
Found C 77.97 H 3.81 N 18.27
Molecular Mass Calcd. 308.1062
Found 308.1059

b) *By Pyrolysis of* **9**: A small sublimation apparatus with 100 mg (0.23 mmol) of **9** was evaporated to 10^{-3} Torr and then dipped into an air-bath preheated to 520°C. After 3 min reaction time the apparatus was cooled, and the sublimate on the cooling finger was purified as described above: 6.4 mg (9%) of **1**, identical with the product obtained according to procedure a).

5,6,8,9-Tetracyano-14,17-dimethoxy-2,11-dithia[3.3]paracyclophane (**10**): In the apparatus described for the synthesis of **8** a solution of 3.64 g (10 mmol) of **5** in methanol/DMF (10:1) and a solution prepared under nitrogen from 1,4-bis(mercaptomethyl)-2,5-dimethoxybenzene[15] and 10 ml of 2 N NaOH in 240 ml of ethanol were dropped synchronously during 10 h into 1.5 l of boiling methanol. After cooling and evaporating to a volume of 200 ml the precipitate formed was filtered off, washed with 20 ml of cold trichloromethane and crystallized from benzonitrile/ethanol: 1.31 g (30%) of **10**, red crystals (dec. > 330°C). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 3.56 and 4.42 (AB, 4H), 3.93 (s, 6H), 4.04 and 4.38 (AB, 4H) 6.86 (s, 2H). – MS: *m/z* = 432 (100%, M^+) a.o.

$C_{22}H_{16}N_4O_2S_2$ (432.5) Calcd. C 61.09 H 3.73 N 12.95 S 14.82
Found C 61.12 H 3.99 N 12.67 S 14.64

5,6,8,9-Tetracyano-14,17-dimethoxy-2,11-dithia[3.3]paracyclophane 2,2,11,11-Tetraoxide (**11**): 600 mg (1.39 mmol) of **10** and 1.2 g (6.95 mmol) of *m*-chloroperbenzoic acid in 1.5 ml of trichloromethane were stirred 6 d at 20°C. The reaction mixture was concentrated by evaporation to a volume of 150 ml; the precipitated disulfone was filtered off, and washed with trichloromethane and methanol, and dried in vacuo: 480 mg (71%) of **11**, dec. > 280°C.

$C_{22}H_{16}N_4O_6S_2$ (496.5) Calcd. C 53.22 H 3.25 N 11.28 S 12.91
Found C 53.42 H 3.25 N 11.32 S 13.18

4,5,7,8-Tetracyano-12,15-dimethoxy[2.2]paracyclophane (**2**): As described for the pyrolysis of **9** to **1**, 500 mg (1.01 mmol) of **11**, in

portions of 100 mg each, was pyrolysed at 520°C/10^{-3} Torr. The collected sublimates were chromatographed on silica from dichloromethane and crystallized from acetonitrile: 29 mg (8%) of **2** in deep-violet crystals of m.p. 313–316°C (dec.). – ^{1}H NMR, MS: see above; X-ray analysis see ref.[2].

$C_{22}H_{16}N_4O_2$ (368.4) Calcd. C 71.73 H 4.38 N 15.21
Found C 71.99 H 4.36 N 15.40
Molecular Mass Calcd. 368.1273
Found 368.1257

5,6,8,9-Tetracyano-14,15,17,18-tetramethyl-2,11-dithia[3.3]paracyclophane (**12**): To 2.26 g (10 mmol) of 1,4-bis(mercaptomethyl)-2,3,5,6-tetramethylbenzene[16] in 40 ml of toluene a mixture of 20 ml of 1 N methanolic KOH and 190 ml of methanol was added under argon. This solution and a solution of 3.62 g (10 mmol) of **5** in 250 ml of methanol/DMF (10:1) were dropped synchronously during 8 h into 1.8 l of boiling methanol. The reaction mixture was concentrated by evaporation in vacuo up to a volume of 200 ml and then added to 400 ml of water. The precipitate was filtered off, washed with water, and dried. The residue was chromatographed from dichloromethane on silica and crystallized from chlorobenzene/ethanol: 880 mg (20.5%) of **12**, deep-yellow crystals (dec. > 325°C). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.39 (s, 12H), 4.19 (s, 4H), 4.27 (s, 4H). – MS: *m/z* (%) = 428 (13, M^+), 191 (100), 159 (42) a.o.

$C_{24}H_{20}N_4S_2$ (428.6) Calcd. C 67.26 H 4.70 N 13.07 S 14.06
Found C 67.31 H 4.83 N 12.90 S 14.82

5,6,8,9-Tetracyano-14,15,17,18-tetramethyl-2,11-dithia[3.3]paracyclophane 2,2,11,11-Tetraoxide (**13**): 500 mg (1.17 mmol) of **12** together with 5 ml of 40% peroxyacetic acid in 30 ml of acetic acid was stirred for 24 h at 20°C. The precipitated disulfone was filtered off, washed with methanol, and dried in vacuo: 475 mg (83%) of **13**, dec. > 270°C.

$C_{24}H_{20}N_4O_4S_2$ (492.6) Calcd. C 58.72 H 4.09 N 11.37 S 13.02
Found C 58.72 H 3.98 N 11.40 S 13.04

4,5,7,8-Tetracyano-12,13,15,16-tetramethyl[2.2]paracyclophane (**3**)

a) *By Photolysis of* **13**: A suspension of 200 mg (0.41 mmol) of **13** in 140 ml of benzonitrile was irradiated under vigorous stirring with a 150 W mercury high-pressure lamp (duran filter) for 2 h. The solvent was distilled off in vacuo; the residue was extracted with trichloromethane, the solution separated from the insoluble by filtration and chromatographed on a short silica column from trichloromethane. Crystallization from acetonitrile yielded 12 mg (8%) of **3**, red crystals, dec. > 340°C. – ^{1}H NMR and MS: see above.

$C_{24}H_{20}N_4$ (364.5) Calcd. C 79.10 H 5.53 N 15.37
Found C 79.30 H 5.39 N 15.41
Molecular Mass Calcd. 364.1688
Found 364.1672

b) *By Pyrolysis of* **13**: In analogy to the synthesis of **1** the pyrolysis of 400 mg (0.81 mmol) of **13** was performed at 500°C/10^{-3} Torr in portions of 100 mg. The pyrolysis products were dissolved in trichloromethane and purified according to procedure a): 80 mg (27%), identical with the product from a).

1,4-Bis(chloromethyl)-2,3,5,6-tetramethoxybenzene: 19.8 g (0.10 mol) of 1,2,4,5-tetramethoxybenzene[17] was added to a mixture of 200 ml of dioxane, 40 ml of 40% aqueous formaldehyde solution and 30 ml of conc. hydrochloric acid, saturated with hydrogen chloride. The mixture was kept for 9 h at 60–70°C with continuous introduction of hydrogen chloride. After cooling 800 ml of ice/water was added; the precipitate was filtered off, dissolved in toluene, filtered through a short silica column, and the solvent was distilled off. Crystallization from methanol yielded 16.5 g (56%) of 1,4-bis-(chloromethyl)-2,3,5,6-tetramethoxybenzene, colourless needles, m.p. 126–127°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 3.95 (s, 12H), 4.69 (s, 4H).

$C_{12}H_{16}Cl_2O_4$ (295.2) Calcd. C 48.82 H 5.46 Cl 24.02
Found C 48.58 H 5.46 Cl 24.17

1,4-Bis(mercaptomethyl)-2,3,5,6-tetramethoxybenzene: 14.7 g (50 mmol) of 1,4-bis(chloromethyl)-2,3,5,6-tetramethoxybenzene and 8.5 g (110 mmol) of thiourea were heated in ethanol 6 h under reflux. By distilling off the solvent the solution was concentrated, and under nitrogen 100 ml of 5 N NaOH was added. After heating 3 h to 100°C and acidification with diluted hydrochloric acid the precipitate was filtered off and crystallized from ethanol: 10.5 g (72%), m.p. 118–119°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.00 (t, 2H), 3.75 (d, 4H), 3.89 (s, 12H).

$C_{12}H_{18}O_4S_2$ (290.4) Calcd. C 49.63 H 6.25 S 22.08
Found C 49.90 H 6.48 S 22.18

5,6,8,9-Tetracyano-14,15,17,18-tetramethoxy-2,11-dithia[3.3]paracyclophane (**14**): In the cyclisation equipment described above solutions of 3.64 g (10 mmol) of **5** in 250 ml of ethanol/DMF (5:1) and of 2.90 g (10 mmol) of 1,4-bis(mercaptomethyl)-2,3,5,6-tetramethoxybenzene in 240 ml of ethanol, to which 10 ml 2 N NaOH was added, were dropped under nitrogen during 12 h into 1.8 l of boiling *tert*-butyl alcohol. By distillation in vacuo the solution was concentrated to a volume of 100 ml, 300 ml of methanol/water (2:1) was added, and the precipitate was filtered off, washed with cold methanol, and dried in vacuo. After chromatography from dichloromethane on silica and crystallization from chlorobenzene/ethanol 690 mg (14%) of **14** (dec. > 300°C) was obtained. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 3.87 (s, 4H), 3.93 (s, 12H), 4.24 (s, 4H). – MS: *m/z* (%) = 492 (100, M^+).

$C_{24}H_{20}N_4O_4S_2$ (492.6) Calcd. C 58.52 H 4.09 N 11.37 S 13.02
Found C 58.47 H 4.18 N 11.22 S 12.92

5,6,8,9-Tetracyano-14,15,17,18-tetramethoxy-2,11-dithia[3.3]paracyclophane 2,2,11,11-Tetraoxide (**15**): A suspension of 500 mg (1.02 mmol) of **14** in 40 ml of acetic acid/trichloromethane (1:1) to which 3 ml of 40% peroxyacetic acid was added was stirred at 20°C for 12 h. The precipitated disulfone was filtered off, washed with methanol, and dried in vacuo: 510 mg (90%), dec. > 280°C. Due to its insolubility **15** was difficult to recrystallize, and therefore it was used for the next reaction without further purification.

$C_{24}H_{20}N_4O_8S_2$ (556.6) Calcd. C 51.79 H 3.62 N 10.07 S 11.52
Found C 51.25 H 3.59 N 9.89 S 11.83

4,5,7,8-Tetracyano-12,13,15,16-tetramethoxy[2.2]paracyclophane (**4**): As described for the synthesis of **1** 400 mg (0.72 mmol) of **15** was pyrolysed in portions of 100 mg each at 520°C/10^{-3} Torr. Chromatography from dichloromethane on silica yielded 58 mg (19%) of **4** in orange-red prisms (from acetonitrile), dec. > 350°C. – ^{1}H NMR, MS: see above; X-ray structure analysis see ref.[2].

$C_{24}H_{20}N_4O_4$ (428.5) Calcd. C 67.28 H 4.71 N 13.08
Found C 67.36 H 4.58 N 13.13
Molecular Mass Calcd. 428.1484
Found 428.1492

6,7,9,10-Tetracyano-3,12-dithia[4.4]paracyclophane (**19**): To 1.98 g (10 mmol) of 1,4-bis(2-mercaptoethyl)benzene[18] in 240 ml of methanol/tetrahydrofuran (3:1) under careful exclusion of oxygen 10 ml of 2 N NaOH was added. This solution and that of 3.64 g (10 mmol) of **5** in 250 ml of methanol/DMF (10:1) were dropped synchronously during 8 h into 1.5 l of boiling methanol. By distilling off the solvents the reaction mixture was concentrated to a

volume of about 50 ml and added to 400 ml of water. The precipitate formed was filtered off, washed with cold methanol, and dried in vacuo. Chromatography on silica from dichloromethane yielded 1.20 g (30%) of **19**, yellow crystals (from acetonitrile), dec. > 320°C. – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.64–2.71 (m, 4H), 3.16–3.21 (m, 4H), 3.89 (s, 4H), 7.03 (s, 4H). – MS: *m/z* (%) = 400 (92, M^+), 104 (100), a.o.

$C_{22}H_{16}N_4S_2$ (400.5) Calcd. C 65.97 H 4.03 N 13.99 S 16.01
Found C 65.78 H 4.10 N 14.01 S 16.05

6,7,9,10-Tetracyano-3,12-dithia[4.4]paracyclophane 3,3,12,12-Tetraoxide (**20**): To a solution of 500 mg (1.25 mmol) of **19** in 1.5 l of trichloromethane 1.0 g (5.8 mmol) of *m*-chloroperoxybenzoic acid was added. After 3 d stirring at 20°C the precipitate was filtered off, washed with trichloromethane and methanol, and dried in vacuo: 480 mg (83%) of **20**, dec. > 220°C.

$C_{22}H_{16}N_4O_4S_2$ (464.5) Calcd. C 56.88 H 3.47 N 12.06 S 13.80
Found C 57.34 H 3.22 N 11.74 S 13.47

5,6,8,9-Tetracyano[3.3]paracyclophane (**16**): 100 mg (0.22 mmol) of **20** was pyrolysed in a pyrolysis apparatus[10] at 10^{-3} Torr; the pyrolysis zone was kept at 580°C, and the temperature of the heating zone was gradually increased from 200 to 400°C. The deposit at the cooling finger was dissolved in dichloromethane and chromatographed on silica. Recrystallization from acetonitrile yielded 8.1 mg (11%) of **16**, yellow needles, m.p. 298–302°C. – ^{1}H NMR and MS: see Theoretical Part.

$C_{22}H_{16}N_4$ (336.4) Calcd. C 78.55 H 4.80 N 16.65
Found C 78.27 H 4.59 N 16.85

6,7,9,10-Tetracyano-16,19-dimethoxy-3,12-dithia[4.4]paracyclophane (**21**): Solutions of 2.58 g (10 mmol) of 1,4-bis(2-mercaptoethyl)-2,5-dimethoxybenzene[18] and 10 ml of 2 N NaOH in 240 ml of methanol/tetrahydrofuran (7:5) as well as of 3.64 g (10 mmol) of **5** in 250 ml of methanol/DMF (10:1) were dropped synchronously within 8 h under nitrogen to 1.5 l of boiling methanol. The solvents were distilled off in vacuo, and the residue was washed with water, sucked off, dissolved in dichloromethane, and filtered over a short silica column. After chromatography from dichloromethane on silica (R_f = 0.45) and recrystallization from benzonitrile: 0.47 g (10%) of **21**, red crystals, m.p. 320 (dec.). – ^{1}H NMR (360 MHz, [D_5]nitrobenzene): δ = 2.44–2.54 (m, 2H), 3.22–3.33 (m, 2H), 3.48–3.58 (m, 2H), 3.76–3.86 (m, 2H), 4.27 and 4.44 (AB, *J* = 15.3 Hz, 4H), 4.17 (s, 6H), 6.92 (s, 2H). – MS: *m/z* (%) = 460 (100, M^+).

$C_{24}H_{20}N_4O_2S_2$ (460.6) Calcd. C 62.59 H 4.38 N 12.17 S 13.92
Found C 62.32 H 4.32 N 12.04 S 13.83

6,7,9,10-Tetracyano-16,19-dimethoxy-3,12-dithia[4.4]paracyclophane 3,3,12,12-Tetraoxide (**22**): To a suspension of 170 mg (0.37 mmol) of **21** in 1 l of trichloromethane/dichloromethane (1:1) 310 mg (1.80 mmol) of *m*-chloroperoxybenzoic acid was added. After stirring for 10 d at 20°C the solvents were distilled off in vacuo, and the precipitate was filtered off, washed with trichloromethane and methanol, and dried in vacuo: 120 mg (62%), dec. > 270°C. Since all attempts to purify **22**, due to the insolubility, did not lead to an analytically pure product, **22** was used for the following reaction without further purification.

$C_{24}H_{20}N_4O_6S_2$ (524.6)
Calcd. C 54.95 H 3.84 N 10.68 S 12.22
Found C 54.64 H 3.87 N 10.91 S 12.76

5,6,8,9-Tetracyano-14,17-dimethoxy[3.3]paracyclophane (**17**): Gas-phase pyrolysis of **22** was performed as described for the preparation of **16**. The crystalline deposit at the cooling finger of the pyrolysis apparatus[10] was dissolved in dichloromethane, chromatographed from dichloromethane on silica, and recrystallized from chlorobenzene: 12.7 mg (11%) of **17**, dark-red crystals, m.p. 330–334°C (dec.). – ^{1}H NMR, MS and X-ray structure analysis: see Theoretical Part.

$C_{24}H_{20}N_4O_2$ (396.4) Calcd. C 72.71 H 5.09 N 14.13
Found C 72.79 H 4.97 N 13.98

1,4-Bis(cyanomethyl)-2,3,5,6-tetramethylbenzene (**26**): 80 g (250 mmol) of **25**[19] was added within 1 h under stirring to a suspension of 29.4 g (600 mmol) of sodium cyanide in 400 ml of dimethyl sulfoxide at 55°C. The stirring was continued for further 2 h at 50°C and then shortly at 85°C. The mixture then was added to 1.5 l of ice/water; the precipitate was filtered off and dried in vacuo: 49.8 g (94%) of **26** of m.p. 256–258°C (from methanol; ref.[20] 269–270°C). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.34 (s, 12H), 3.71 (s, 4H). – MS: *m/z* (%) = 212 (100, M^+).

$C_{14}H_{16}N_2$ (212.3) Calcd. C 79.20 H 7.60 N 13.20
Found C 79.04 H 7.65 N 13.32

2,3,5,6-Tetramethyl-1,4-benzenediacetic Acid (**27**) *and its Dimethyl Ester* (**28**): 41.7 g (196 mmol) of **26** in 600 ml of 50% sulfuric acid was heated 9 h under reflux. After cooling the reaction mixture was poured into 3 l of ice/water, the precipitate was filtered off, washed with water, dissolved in 6 N NaOH and boiled for 10 min with active charcoal. After acidification with diluted hydrochloric acid the precipitate was filtered off, washed with water, and dried in vacuo: 43.3 g (88%) of hardly soluble **27** which, without further purification, was esterified: the suspension of **27** in 900 ml of tetrahydrofuran/methanol (5:4) after addition of 3.8 ml of conc. sulfuric acid was heated 16 h under reflux. The solvents were distilled off, and the residue was washed with water and then dissolved in trichloromethane. After washing with aqueous sodium hydrogen carbonate solution and with water and drying (sodium sulfate) the solvent was distilled off: 33.1 g (69%) of **28**, colourless needles of m.p. 116–118°C (from ligroin). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.24 (s, 12H), 3.68 (s, 6H), 3.75 (s, 4H).

$C_{16}H_{22}O_4$ (278.3) Calcd. C 69.04 H 7.97
Found C 69.32 H 7.90

1,4-Bis(2-hydroxyethyl)-2,3,5,6-tetramethylbenzene (**29**): A solution of 33.0 g (119 mmol) of **28** in 600 ml of tetrahydrofuran was added at 20°C within 5 h to a suspension of 10.0 g (264 mmol) of $LiAlH_4$ in 400 ml of tetrahydrofuran. After 1 h further stirring excess of $LiAlH_4$ was hydrolysed by adding water dropwise. Acidification with diluted hydrochloric acid, extraction with trichloromethane, washing of the extract with water, drying over sodium sulfate, and evaporation of the solvent in vacuo led to 26.1 g (98%) of **29**, colourless needles, m.p. 169–170°C (from toluene). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.50 (s, 2H), 2.28 (s, 12H), 2.90–3.15 (m, 4H), 3.63–3.88 (m, 4H).

$C_{14}H_{22}O_2$ (222.3) Calcd. C 75.63 H 9.98
Found C 75.70 H 9.78

1,4-Bis(2-bromoethyl)-2,3,5,6-tetramethylbenzene (**30**): To a solution of 26.1 g (117 mmol) of **29** in 800 ml of dichloromethane 105 g (317 mmol) of tetrabromomethane and 104 g (397 mmol) of triphenylphosphane were added, and the reaction mixture was stirred at 20°C for 12 h. After evaporation of the solvents *in vacuo* the residue was given into 500 ml of methanol and stirred for 1 h. The precipitate was filtered off and dried in vacuo: 36.2 g (88%) of **30**, m.p. 194–195.5°C (from ligroin/ethanol 2:1). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.25 (s, 12H), 3.30 (s. 8H).

$C_{14}H_{20}Br_2$ (348.1) Calcd. C 48.30 H 5.79 Br 45.91
Found C 48.10 H 5.60 Br 46.04

1,4-Bis(2-mercaptoethyl)-2,3,5,6-tetramethylbenzene (**31**): 36.1 g (104 mmol) of **30** and 18 g (236 mmol) of thiourea in 800 ml of 2-methoxyethanol were heated under reflux for 3 h. The solvent was distilled off in vacuo, and the residue after addition of a solution of 84.1 g (2.10 mol) of sodium hydroxide in 800 ml of water was heated under nitrogen for 10 h under reflux. Acidification with hydrochloric acid, extraction with trichloromethane, washing and drying of the extract, and evaporation of the solvent yielded 26.3 g (99%) of **31** of m.p. 139–141°C. After filtration from dichloromethane through silica and recrystallization from benzene: colourless crystals, m.p. 149–151°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.50 (s, 2H), 2.23 (s, 12H), 2.50–2.75 (m, 4H), 2.85–3.13 (m, 4H).

$C_{14}H_{22}S_2$ (254.4) Calcd. C 66.08 H 8.72 S 25.20
Found C 65.85 H 8.89 S 24.87

6,7,9,10-Tetracyano-16,17,19,20-tetramethyl-3,12-dithia[4.4]paracyclophane (**23**): 1.27 g (5.0 mmol) of **31** was dissolved under nitrogen in a mixture of 5 ml of 2 N NaOH, 195 ml of 2-methoxyethanol and 300 ml of dioxan. This solution and the solution of 1.82 g (5.0 mmol) of **5** in 500 ml of 2-methoxyethanol/DMF (50:1) were synchronously dropped during 8 h to 1.5 l of boiling 2-methoxyethanol. The residue obtained by evaporation of the solvents in vacuo was dissolved in trichloromethane, the solution was washed with water and filtered through a short silica column. Chromatography from dichloromethane on silica and recrystallization from benzonitrile/ethanol (1:1) yielded 0.37 g (16%) of **23**, yellow crystals, m.p. 304–308°C (dec.). – ^{1}H NMR (360 MHz, [D_2]dichloromethane): δ = 2.26 (s, 12H), 2.88–2.91 (m, 4H), 3.21–3.23 (m, 4H), 3.90 (s, 4H). – MS: *m/z* (%) = 456 (100, M^+).

$C_{26}H_{24}N_4S_2$ (456.6) Calcd. C 68.39 H 5.30 N 12.27 S 14.04
Found C 68.27 H 5.38 N 12.17 S 13.83

6,7,9,10-Tetracyano-16,17,19,20-tetramethyl-3,12-dithia[4.4]paracyclophane 3,3,12,12-Tetraoxide (**24**): 250 mg (0.55 mmol) of **23** in 350 ml of dichloromethane after addition of 440 mg (2.54 mmol) of *m*-chloroperoxybenzoic acid was stirred at 20°C for 1 d. The precipitate was filtered off, washed with methanol, and dried in vacuo: 250 mg (87%) of **24**, dec. > 310°C. The product was used for the pyrolysis to **18** without further purification.

$C_{26}H_{24}N_4O_4S_2$ (520.6) Calcd. C 59.98 H 4.65 N 10.76 S 12.32
Found C 59.60 H 4.28 N 10.39 S 12.78

5,6,8,9-Tetracyano-14,15,17,18-tetramethyl[3.3]paracyclophane (**18**): 100 mg (0.19 mmol) of **24** was pyrolysed in an integrated sublimation/pyrolysis equipment with automatic temperature control[10] at 10^{-3} Torr and 580°C in the pyrolysis zone with the temperature of the sublimation zone increasing from 200 to 400°C. The product separated on the cooling finger was dissolved in dichloromethane, chromatographed on silica, and crystallized from acetonitrile: 13.3 mg (18%) of **18**, orange-yellow crystals, m.p. > 354°C (dec.). – ^{1}H NMR and MS: see above.

$C_{26}H_{24}N_4$ (392.5) Calcd. C 79.56 H 6.16 N 14.28
Found C 79.47 H 6.36 N 14.06

7,8,10,11-Tetracyano-4,13-dithia[5.5]paracyclophane (**34**): Solutions of 2.26 g (10 mmol) of 1,4-bis(3-mercaptopropyl)benzene[13] in 10 ml 2 N NaOH and 240 ml of methanol/dioxan (9:1) and of 3.64 g (10 mmol) of **5** in 250 ml of methanol/DMF (25:1) were dropped under nitrogen synchronously within 6 h to 1.5 l of boiling methanol. The solvents were distilled off in vacuo, and the residue was triturated with water, filtered off, dissolved in dichloromethane and chromatographed on silica from dichloromethane. After crystallization from acetonitrile: 1.40 g (33%) of **34**, yellow crystals, dec. > 234°C. – ^{1}H NMR (80 MHz, [D_2]dichloromethane): δ = 1.70–2.20 (m, 8H), 2.53–2.78 (m, 4H), 4.05 (s, 4H), 7.01 (s, 4H). – MS: *m/z* (%) = 428 (100, M^+).

$C_{24}H_{20}N_4S_2$ (428.6) Calcd. C 67.26 H 4.70 N 13.07 S 14.96
Found C 67.42 H 4.95 N 12.99 S 14.95

7,8,10,11-Tetracyano-4,13-dithia[5.5]paracyclophane 4,4,13,13-Tetraoxide (**35**): 1.00 g (2.33 mmol) of **34** was stirred for 5 d at 20°C with 2.00 g (11.6 mmol) of *m*-chloroperoxybenzoic acid in 300 ml of dichloromethane. Concentration of the solution to a volume of 100 ml, filtering off the precipitate, washing it with dichloromethane and methanol, and drying in vacuo resulted in 0.98 g (85%) of **35** which without further purification was used for the pyrolysis experiment.

6,7,9,10-Tetracyano[4.4]paracyclophane (**32**): 200 mg (0.40 mmol) of **35** was pyrolysed in the pyrolysis apparatus[10] at 10^{-3} Torr and a pyrolysis zone temperature of 580°C; the temperature of the sublimation zone was gradually increased from 200 to 400°C. The deposit on the cooling finger was dissolved in dichloromethane and purified by chromatography on silica from dichloromethane and recrystallization from acetonitrile: 40.1 mg (27%) of **32**, colourless needles, dec. > 360°C. – ^{1}H NMR and MS: see above.

$C_{24}H_{20}N_4$ (364.4) Calcd. C 79.09 H 5.53 N 15.37
Found C 79.21 H 5.65 N 15.17

1,4-Bis(3-mercaptopropyl)-2,5-dimethoxybenzene: 30.0 g (80.2 mmol) of 1,4-bis(3-bromopropyl)-2,5-dimethoxybenzene[14] and 14.0 g (184 mmol) of thiourea were heated in 500 ml of ethanol 3 h under reflux. The residue obtained by evaporation of the solvent in vacuo was dissolved under nitrogen in a mixture from 64.0 g (1.60 mmol) of aqueous sodium hydroxide and 500 ml of water and heated for 6 h under reflux. After cooling the solution was acidified with diluted hydrochloric acid and extracted with dichloromethane. On evaporation of the solvent in vacuo 20.7 g (90%) of the product crystallized, m.p. 59–60°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.40 (t, *J* = 7.6 Hz, 2H), 1.75–2.12 (m, 4H), 2.38–2.80 (m, 8H), 3.78 (s, 6H), 6.65 (s, 2H). – MS: *m/z* (%) = 286 (100, M^+).

$C_{14}H_{22}O_2S_2$ (286.4) Calcd. C 59.97 H 5.75 S 22.87
Found C 59.78 H 5.98 S 22.99

7,8,10,11-Tetracyano-18,21-dimethoxy-4,13-dithia[5.5]paracyclophane (**36**): In the cyclisation apparatus described before solutions of 3.64 g (10 mmol) of **5** in 250 ml of methanol/DMF (10:1) and of 2.80 g (10 mmol) of 1,4-bis(3-mercaptopropyl)-2,5-dimethoxybenzene in a mixture of 10 ml of 2 N NaOH and 240 ml of methanol/tetrahydrofuran (5:1) were dropped under nitrogen within 6 h to 1.5 l of boiling methanol. The residue obtained by evaporation of the solvent was washed with water and dissolved in dichloromethane. Chromatography on silica from dichloromethane and crystallization from acetonitrile yielded 1.00 g (20.5%) of **36**, red crystals of m.p. 238°C. – ^{1}H NMR (360 MHz, [D_2]dichloromethane): δ = 1.65–1.75 (m, 2H), 1.89–2.02 (m, 4H), 2.22–2.27 (m, 2H), 2.31–2.37 (m, 2H), 3.04–3.10 (m, 2H), 3.78 (s, 6H), 4.02 and 4.10 (AB, *J* = 14.5 Hz, 4H), 6.60 (s, 2H). – MS: *m/z* (%) = 488 (100, M^+).

$C_{26}H_{24}N_4O_2S_2$ (488.6) Calcd. C 63.91 H 4.95 N 11.47 S 13.12
Found C 63.75 H 4.84 N 11.70 S 12.88

7,8,10,11-Tetracyano-18,21-dimethoxy-4,13-dithia[5.5]paracyclophane 4,4,13,13-Tetraoxide (**37**): 440 mg (0.90 mmol) of **36** was stirred in 250 ml of dichloromethane after addition of 770 mg of *m*-chloroperoxybenzoic acid for 4 d at 20°C. The precipitate formed was filtered off, washed with dichloromethane and methanol, and dried in vacuo: 460 mg (93%) of **37**. In spite of several recrystalli-

zation attempts a correct analysis was not obtained. The product was used directly for the pyrolysis reaction.

$C_{26}H_{24}N_4O_6S_2$ (552.6) Calcd. C 56.51 H 4.38 N 10.14 S 11.60
Found C 56.88 H 4.02 N 10.49 S 12.06

6,7,9,10-Tetracyano-16,19-dimethoxy[4.4]paracyclophane (**33**): 100 mg (0.18 mmol) of **37**, in analogy to the previously described sulfone pyrolyses, was pyrolysed at 560°C/10^{-3} Torr; sublimation zone temperature was gradually raised from 200 to 400°C. The pyrolysis product deposited on the cooling finger was dissolved in dichloromethane. Evaporation yielded a residue which was purified by preparative layer chromatography (silica 60-F_{254} of Merck, dichloromethane) and recrystallization from acetonitrile: 15.9 mg (21%) of **33**, orange-red crystals, dec. > 330°C. – ^{1}H NMR and MS: see above.

$C_{26}H_{24}N_4O_2$ (424.5) Calcd. C 73.56 H 5.70 N 13.20
Found C 73.66 H 5.77 N 13.12

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1: 105537-09-5 / **2**: 105537-10-8 / **3**: 105537-11-9 / **4**: 105537-12-0 / **5**: 105537-13-1 / **6**: 80717-49-3 / **7**: 23488-38-2 / **8**: 105537-14-2 / **9**: 105537-15-3 / **10**: 105537-16-4 / **11**: 105537-17-5 / **12**: 105562-21-8 / **13**: 105537-18-6 / **14**: 105537-19-7 / **15**: 105537-20-0 / **16**: 105537-21-1 / **17**: 105537-22-2 / **18**: 105537-23-3 / **19**: 105537-24-4 / **20**: 105537-25-5 / **21**: 105562-22-9 / **22**: 105537-26-6 / **23**: 105562-23-0 / **24**: 105537-27-7 / **25**: 35168-64-0 / **26**: 1675-71-4 / **27**: 15657-67-7 / **28**: 18773-19-8 / **29**: 15657-69-9 / **30**: 105537-28-8 / **31**: 105537-29-9 / **32**: 105537-30-2 / **33**: 105537-31-3 / **34**: 105537-32-4 / **35**: 105537-33-5 / **36**: 105537-34-6 / **37**: 105537-35-7 / 1,4-bis(mercaptomethyl)benzene: 105-09-9 / 1,2,4,5-tetramethoxybenzene: 2441-46-5 / formaldehyde: 50-00-0 / 1,4-bis(mercaptomethyl)-2,5-dimethoxybenzene: 50874-28-7 / 1,4-bis(mercaptomethyl)-2,3,5,6-tetramethylbenzene: 10519-84-3 / 1,4-bis(mercaptomethyl)-2,3,5,6-tetramethoxybenzene: 105537-36-8 / 1,4-bis(chloromethyl)-2,3,5,6-tetramethoxybenzene: 106468-90-0 / 1,2,4-tricyano-3,6-dimethylbenzene: 80717-50-6 / 1,4-bis(2-mercaptoethyl)benzene: 3998-55-8 / 1,4-bis(2-mercaptoethyl)-2,5-dimethoxybenzene: 64746-03-8 / 1,4-bis(3-mercaptopropyl)benzene: 68712-38-9 / 1,4-bis(3-bromopropyl)-2,5-dimethoxybenzene: 78975-98-1 / 1,4-bis(3-mercaptopropyl)-2,5-dimethoxybenzene: 105537-37-9

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