

SYNTHESES AND REACTIONS OF SOME NEW DITHIA[3.1.3.1]PARACYCLOPHANES
AND [2.1.2.1]PARACYCLOPHANES

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Abstract - The syntheses of new dithia[3.1.3.1]paracyclophanes and [2.1.2.1]paracyclophanes are presented and their NMR spectroscopic properties are described. The possibility to synthesize new twin paracyclophanes by intramolecular coupling reactions of these cyclophanes is discussed.

The syntheses of cyclophanes with more than two aromatic rings and the study of their chemical, physical and spectroscopic properties have received considerable attention during the past few years.¹⁻¹⁵ The main interest often was focussed on cyclophanes corresponding to nonfunctional hydrocarbons. However, the synthesis of cyclophanes bearing functional groups in the bridges and the study of the resulting structural, spectroscopic and chemical properties is one interesting aspect in cyclophane chemistry.

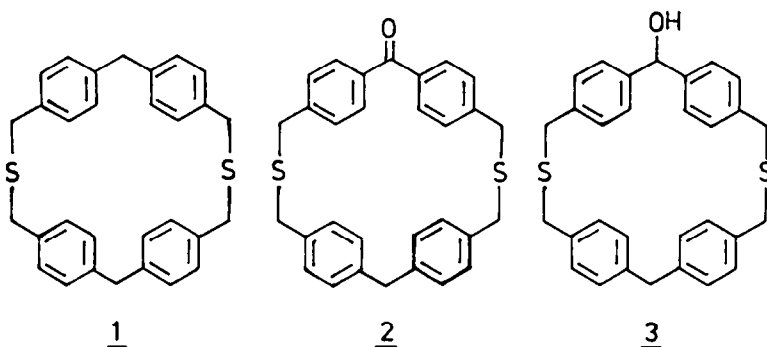


Figure 1

In connection with investigations about new twin cyclophanes¹⁶ we synthesized the 2,18-dithia-[3.1.3.1]paracyclophanes 1, 2, and 3 (Figure 1), and the [2.1.2.1]paracyclophanes 5, 6, and 7 (Figure 2) bearing functional groups in the shorter bridges. Furthermore, the already known parent hydrocarbon [2.1.2.1]paracyclophane (4)³ was now synthesized by a new synthetic route via the 2,18-dithia[3.1.3.1]paracyclophane (1) and subsequent photolysis in trimethylphosphite. R.H. Mitchell and Y.-H. Lai have shown^{10,11} that in the case of related [2.1.2.1]metacyclophanes, twin cyclophanes are not accessible by an intramolecular reaction between the short bridges (between carbon atoms 9 and 24, respectively). The authors conceive this coupling reaction impossible for stereochemical reasons.

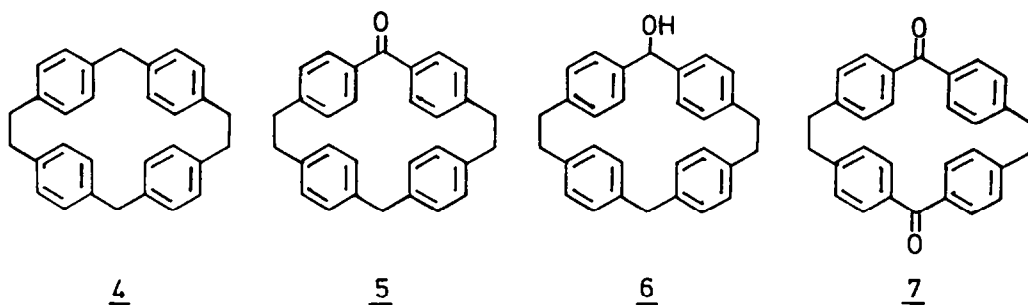
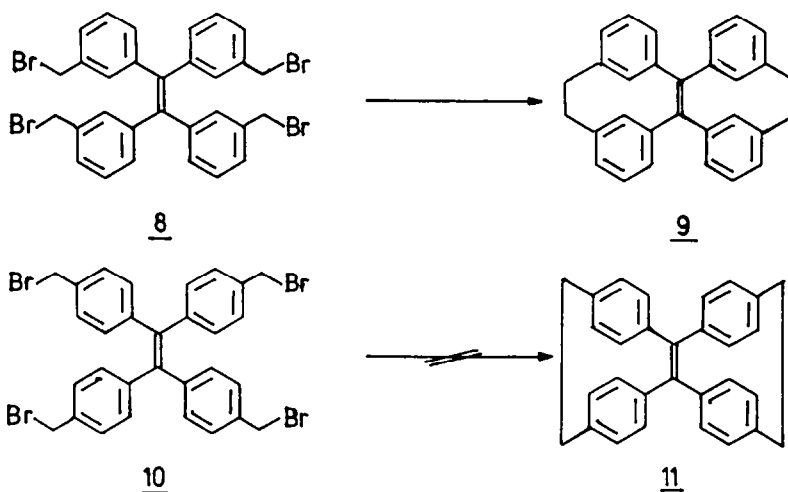


Figure 2

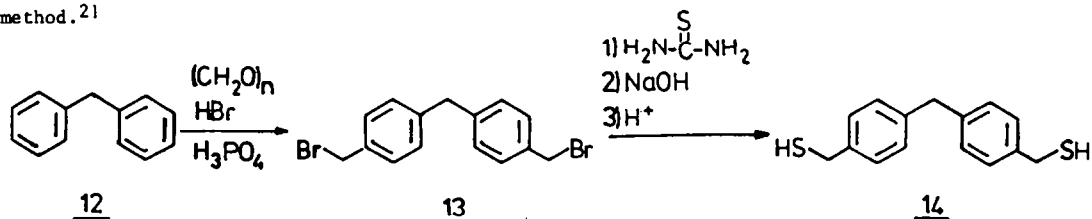
We reported in an earlier publication¹⁶ the twofold phenyllithium coupling of tetrakis[(3-bromomethyl)phenyl]ethene (8) to the first twin cyclophane 9. By the same coupling conditions tetrakis[(4-bromomethyl)phenyl]ethene (10)⁵ did not yield the corresponding twin paracyclophane 11.



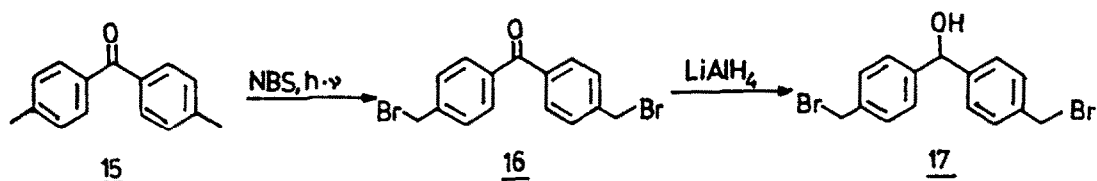
For this reason, [2.1.2.1]paracyclophanes 5 - 7 were prepared as possible precursors of 11. We were especially interested in the synthesis of [2.1.2.1]paracyclophane-9,24-dione (7) and in the study of its behaviour under coupling conditions of the McMurry reaction.¹⁷⁻¹⁹

SYNTHESES

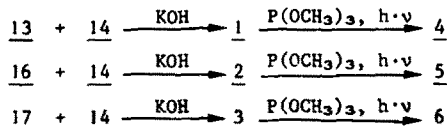
The dithia[3.1.3.1]paracyclophanes 1 - 3 were synthesized as follows: Bromomethylation of diphenylmethane (12) following the procedure of D.J. Cram et al.²⁰ gives bis(4-bromomethylphenyl)methane (13) in 40% yield. 13 is converted to bis(4-mercaptomethylphenyl)methane (14) by the thiourea method.²¹



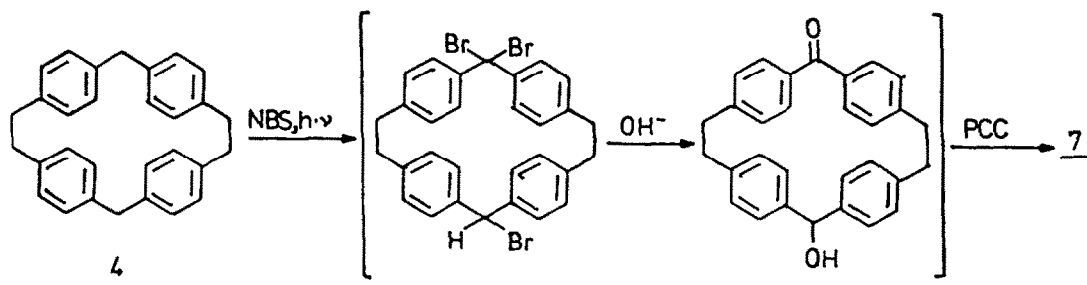
4,4'-Dimethylbenzophenone (15) is easily photobrominated with NBS in CCl_4 at room temperature to give bis(4-bromomethyl)benzophenone (16)^{22,23} which is reduced with LiAlH_4 to bis(4-bromomethylphenyl)methane (17).



Reaction of 13 with 14, 14 with 16, and 14 with 17, respectively, in ethanol under dilution conditions and KOH as the base, results in the dithia[3.1.3.1]paracyclophanes 1, 2, and 3, with yields of 45%, 47%, and 40%, respectively. The dithia[3.1.3.1]paracyclophanes 1 - 3 are desulfurized by photolysis in trimethylphosphite to give 4, 5, and 6:



The 2,18-dithia[3.1.3.1]paracyclophane-10,26-dione (18) has already been described.^{22,23} However, in our hands the synthesis of the desired [2.1.2.1]paracyclophane-9,24-dione (7) via its sulfur containing precursor was not successful because bis(4-mercaptomethyl)benzophenone (19) is very sensitive to oxidation and could not be prepared from 16. 7 can be prepared from 4 as follows: 4 is brominated with threefold excess of NBS in CCl₄ at room temperature. The bromination product is hydrolyzed in wet THF in the presence of K₂CO₃, and the crude hydrolysis product is oxidized in dry dichloromethane with pyridinium chlorochromate to give 7 in 20% yield:



Reactions of the [2.1.2.1]paracyclophanes 5 and 7

The reductive coupling of carbonyl compounds to unsaturated products by low valent titanium (McMurry reaction) has been used successfully in a wide range of syntheses.²⁴ J.E. McMurry and co-workers showed that even highly substituted aldehydes and ketones react in good yield to the corresponding alkenes. In addition, even cyclophanes were prepared in good yields by intra- or intermolecular coupling of appropriate precursors.²⁵

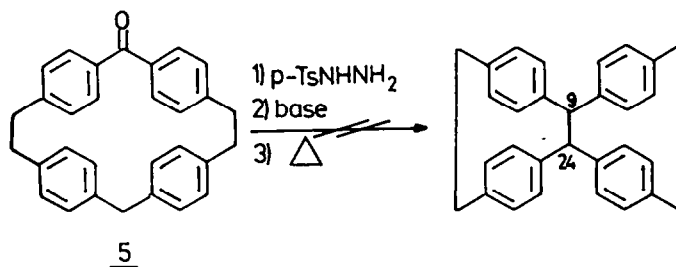
In this connection we were interested in studying the coupling behaviour of the diketones 7; if the two carbonyl functions approach each other close enough, an intramolecular coupling should be possible. On the other hand, dimerization and trimerization of 7 by the McMurry reactions would also be an interesting possibility.

For this purpose, a coupling reagent was prepared from zinc and TiCl₄ in THF. Over a period of 24 hours small amounts of 7 were added to the boiling THF mixture. However, coupling products from inter- or intramolecular reactions were not detected, and only unreacted 7 was recovered.

In a second experiment the coupling reagent was prepared by the reaction of Zn/Cu with TiCl₄ in 1,2-dimethoxyethane. 7 was added over 48 hours to the mixture in boiling DME. After workup, [2.1.2.1]paracyclophane (4) was isolated but no coupling products were observed.

The Bamford-Stevens reaction is another useful synthetic method to form carbon-carbon links. A variety of multibridged cyclophanes and even the legendary "superphane" were synthesized using this reaction.²⁶ Hence, the monoketone 5 was treated with p-toluenesulfonyl hydrazide and p-toluene-

sulfonic acid as catalyst yielding the corresponding tosylhydrazone. Treatment of the crude product with base and subsequent heating yielded a complex mixture in which no products were detected indicating a central bond formation between C-9 and C-24.



NMR PROPERTIES OF THE CYCLOPHANES 1 - 7

The 300 MHz $^1\text{H-NMR}$ data of the cyclophanes 1 - 7 are summarized in Table 1. The spectra of the cyclophanes synthesized here show a high field shift for absorptions of the aromatic hydrogen atoms typical forphanes of comparable size. As expected this effect is less distinct in the case of the dithia[3.1.3.1]paracyclophanes 1, 2, and 3 compared to the [2.1.2.1]paracyclophanes 4, 5, 6, and 7 with shorter bridges. The hydrogens of the CH_2 groups of the three-membered thiabridges

Table 1 : 300 MHz $^1\text{H-NMR}$ spectra of the cyclophanes 1 - 7 (δ , ppm)

	ArH	$\text{ArCH}_2\text{CH}_2\text{Ar}$	$\text{ArCH}_2\text{-S}$	ArCH_2Ar	ArCHOAr	ArCHOAr
<u>1</u>	6.98-6.84, m, (AA'BB'), 16H,	-	3.69, s, 8H,	3.92, s, 4H,	-	-
<u>2</u>	7.49-6.83, m, (2xAA'BB'), 16H,	-	3.85, s, 4H, 3.73, s, 4H,	3.88, s, 2H,	-	-
<u>3</u>	7.16-6.83, m, (2xAA'BB'), 16H,	-	3.69, s, 8H,	3.92, s, 2H,	5.27, d, 4 Hz, 1H,	2.07, d, 4 Hz, 1H,
<u>4</u>	6.82-6.53, m, (AA'BB'), 16H,	2.83, s, 8H,	-	3.79, s, 2H,	-	-
<u>5</u>	7.10-6.54, m, (2xAA'BB'), 16H,	2.85-2.80, m, (AA'BB'), 8H,	-	3.91, s, 2H,	-	-
<u>6</u>	6.95-6.53, m, (2xAA'BB'),	2.85, s, 8H,	-	-	5.69, d, 4 Hz, 1H,	1.95, d, 4 Hz, 1H,
<u>7</u>	7.29-6.63, m, (AA'BB'), 16H,	2.93, s, 8H,	-	-	-	-

in the dithiaphanes 1 and 3 are singlets, whereas in the case of 2 two signals are observed at 3.76 and 3.85 ppm. The H-atoms of the methylene groups in the two-membered bridges of 5 give rise to two signal groups (AA'BB'-system, Figure 3), whereas in the [2.1.2.1]paracyclophanes 4, 6 and 7 only singlets are found for the corresponding protons. The signals for the H-atoms of the methylene groups of the diphenylmethane units appear at about 3.9 ppm in the case of the dithiacyclophanes, and at about 3.8 ppm in the case of the corresponding [2.1.2.1]paracyclophanes. No temperature dependence of the spectra of the cyclophanes 1 - 7 is observed in the range of -50° to $+50^\circ\text{C}$. This shows that in this temperature range the molecules are conformationally mobile.

The assignment of the aromatic signals of [2.1.2.1]paracyclophane-9-one (5) (Figure 3) to the benzophenone and the diphenylmethane part of the molecule can be made easily by comparison with the spectra of 4 and 7. The signal groups at about 7.08 and 6.55 ppm can be assigned to the benzophenone part, and the signals at 6.93 und 6.68 ppm to the diphenylmethane unit.

More informations about the structures and the conformations of the [2.1.2.1]paracyclophanes can be derived from NOE measurements. The following results were obtained by the NOE experiment with 5.

Irradiation into the frequency of the methylene group of the diphenylmethane unit results in an increase of the signals at about 6.93 ppm, and irradiation into the frequency of the two-membered bridges increases the signals at 6.55 and 6.68 ppm. This proves that the aromatic hydrogens neighbouring the two-membered bridges are especially shifted to high field. The reason for this distinct effect must be the ring currents of the two aromatic rings facing each other. Inspection of models show that a "crown-like" structure is the most probable conformation (see Figure 4).

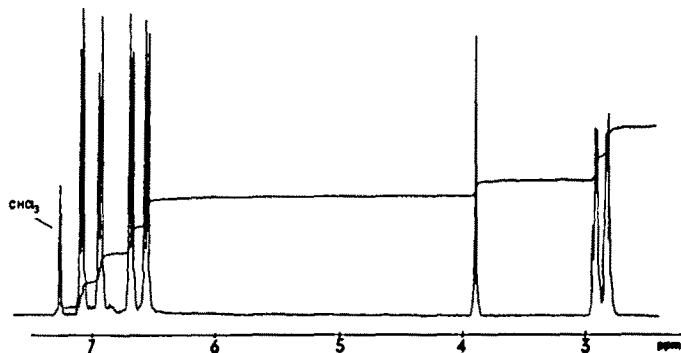


Figure 3 : NMR spectrum of 5

This conformation agrees with the observed order of the shifts of the H-atoms of the aromatic groups in the $^1\text{H-NMR}$ spectra because of a much shorter distance between both rings at the side of the C_2 bridge. As one can see in Figure 4, the carbon atoms 9 and 24 are far apart from one another making an intramolecular coupling reaction to the desired twin cyclophane unfavourable.

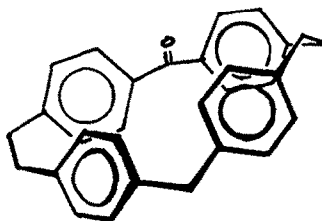


Figure 4

CONCLUSIONS

The 2,18-dithiaparacyclophanes 1, 2, and 3 were synthesized for the first time. It is shown that 1, 2, and 3 can be easily desulfurized to the [2.1.2.1]paracyclophanes 4, 5, and 6, respectively. Furthermore, a synthesis for [2.1.2.1]paracyclophane-9,24-dione 7 was developed by bromination of 4 at the central CH_2 -groups followed by hydrolysis and oxidation. Intramolecular coupling of 5 and 7 to twin cyclophanes by the Bamford-Stevens reaction and the McMurry reaction, respectively, is not possible. NMR studies of the paracyclophanes 4 - 7 indicate that these intramolecular reactions are not possible due to stereochemical reasons.

EXPERIMENTAL

The melting points were determined on an Electrothermal[®] melting point apparatus and are uncorrected. The 60 MHz $^1\text{H-NMR}$ spectra were determined in CDCl_3 on a Bruker EM 360 spectrometer. The 300 MHz $^1\text{H-NMR}$ spectra were recorded on a Bruker AM 300 spectrometer. The IR spectra were obtained with a Perkin Elmer model 377 IR spectrophotometer. Mass spectra were determined on a Varian MAT 311 mass spectrometer using electron impact at 70 eV. The exact mass determination was performed with the same spectrometer using a resolution of $m/\Delta m = 6000$.

Bis(4-mercaptomethylphenyl)methane (14)

5 g (14.1 mmol) of bis(4-bromomethylphenyl)methane (13) and 2.3 g (30.2 mmol) thiourea were dissolved in 70 ml ethanol. This mixture was refluxed for 16 hours. After cooling the solution was concentrated to half of its volume and diluted with ether. During cooling, a salt separated (6.14 g) which was filtered with a Büchner funnel and dried. The salt was refluxed in 200 ml 2N NaOH solution under nitrogen atmosphere for two hours. The alkaline solution was washed with ether (N_2), acidified with conc. HCl and reextracted with ether. The latter ether extracts were com-

bined, dried over Na_2SO_4 , and concentrated to 50 ml. The product crystallized from this solution as colourless needles (2.38 g, 65%), mp 81°C. $^1\text{H-NMR}$ (60 MHz): 7.30 - 6.90 ppm (m, 8H, ArH), 3.90 ppm (s, 2H, ArCH_2Ar), 3.65 ppm (d, 4H, $J = 8$ Hz, ArCH_2S), 1.70 ppm (t, 2H, $J = 8$ Hz, SH); IR (KBr) 3060 (w), 2930 (w), 1510 (m), 1430 (m), 1250 (m), 830 (s) cm^{-1} ; MS: m/z (rel. intensity) 260 (M^+ , 46), 227 (100), 193 (16), 178 (20), 165 (15), 137 (8). Anal. calc. for $\text{C}_{15}\text{H}_{16}\text{S}_2$ C 69.18; H 6.19. Found C 69.07; H 6.01%.

Bis(4-bromomethyl)benzophenone (16)

10 g (47.6 mmol) 4,4'-dimethylbenzophenone (15) was suspended in 250 ml dry tetrachloromethane, and 17 g (95.5 mmol) N-bromosuccinimide was added. The stirred mixture was irradiated with a 500 W photolamp keeping the reaction temperature below 40°C (reaction time 2-3 h). After the end of the reaction the suspension was filtered and concentrated in vacuo to 100 ml. On cooling the product crystallized as colourless crystals. The dibromide was filtered by suction and washed with CCl_4 . Recrystallization from CCl_4 yielded 9.5 g (54%), mp 121°C. $^1\text{H-NMR}$ (60 MHz): 8.00-7.30 ppm (m, 8H, ArH), 4.50 ppm (s, 4H, CH_2Br); IR (KBr) 1660 (m), 1600 (m), 1430 (m), 1280 (m), 9.30 (m) cm^{-1} ; MS: m/z (rel. intensity) 368 (M^+ , 22, correct isotope pattern), 289 (87), 287 (84), 259 (17), 209 (15), 180 (100). Anal. calc. for $\text{C}_{15}\text{H}_{12}\text{Br}_2\text{O}$ C 48.95; H 3.29. Found C 48.75; H 3.50%.

Bis(bromomethylphenyl)methanol (17)

4 g (10.9 mmol) 16 was suspended in 150 ml of dry diethyl ether, and 115 mg (3 mmol) LiAlH_4 was added in small portions to the stirred mixture. After 2 hours the reaction mixture was hydrolyzed with ice water and acidified with 2M sulfuric acid. The ether layer was separated, and the aqueous phase was extracted with ether for several times. The combined ethereal extracts were washed (brine), dried (Na_2SO_4), filtered and evaporated in vacuo. Crystallization from CCl_4 gave colourless crystals. 2.49 g (62%), mp 99°C. $^1\text{H-NMR}$ (60 MHz): δ 7.35 ppm (s, 8H, ArH), 5.80 ppm (s, 1H, CHOH), 4.43 ppm (s, 4H, CH_2Br). IR (KBr) 3500-3100 (w), 1610 (m), 1510 (m), 1420 (m), 1050 (s), 830 (s) cm^{-1} ; MS: m/z (rel. intensity) 370 (M^+ , 6, correct isotope pattern), 291 (37), 289 (64), 199 (94), 197 (99), 118 (88), 91 (100). HRMS calc. for $\text{C}_{15}\text{H}_{14}\text{OBr}_2$ 369.9392. Found 369.9393 \pm 0.001.

2,18-Dithia[3.1.3.1]paracyclophane (1)

3 g (8.47 mmol) bis(4-bromomethylphenyl)methane 13 and 2.2 g (8.47 mmol) bis(4-mercaptomethylphenyl)methane 14 was dissolved in 250 ml of a benzene/ethanol 1:1 mixture and was added simultaneously over a period of 20 hours under nitrogen into 1.5 l of a solution of 1.5 g (26.7 mmol) KOH in ethanol (N_2 purged). Then the solution was stirred one additional hour. Most of the solvent was removed under reduced pressure, and 250 ml of water was added. The aqueous layer was extracted with dichloromethane several times, and the combined CH_2Cl_2 extracts were dried over Na_2SO_4 . This mixture was heated on a water bath and filtered hot. The filtered solution was concentrated to 100 ml. From this solution, 1 crystallized in white needles. Recrystallization from CH_2Cl_2 yielded 1.73 g (45%) of 1. $^1\text{H-NMR}$ (300 MHz) see above. IR (KBr) 1510 (m), 1420 (m), 1100 (m), 820 (s), 730 (s), 720 (s), 590 (s) cm^{-1} . MS: m/z (rel. intensity) 452 (M^+ , 95), 225 (39), 195 (100), 165 (36), 104 (32), 91 (42). HRMS calc. for $\text{C}_{30}\text{H}_{28}\text{S}_2$ 452.1632. Found 451.1645 \pm 0.001.

2,18-Dithia[3.1.3.1]paracyclophane-10-one (2)

A solution of 3 g (8.2 mmol) bis(4-bromomethyl)benzophenone 16 and 2.1 g (8.2 mmol) bis(4-mercaptomethylphenyl)methane 14 in 250 ml of a 1:1 mixture from benzene and ethanol was added under nitrogen over a period of 48 hours to a solution of 1.5 g KOH in 1.5 l ethanol (N_2 purged). After the end of the reaction, the mixture was concentrated in vacuo to 100 ml, hydrolyzed and extracted four times with 150 ml portions of CH_2Cl_2 . The combined extracts were dried over Na_2SO_4 , heated on a water bath, and filtered. This solution was concentrated to about 100 ml. On cooling, 2 separated as a colourless product. Recrystallization from CH_2Cl_2 yielded 1.74 g (47%) of 2, mp 278-280 °C. $^1\text{H-NMR}$ (300 MHz) see above. IR (KBr) 3040 (w), 2920 (w), 1650 (m), 1600 (s), 1420 (m), 1280 (m), 730 (s) cm^{-1} . MS: m/z (rel. intensity) 466 (M^+ , 100), 420 (13), 225 (80), 195 (78), 180 (40), 178 (49), HRMS calc. for $\text{C}_{30}\text{H}_{26}\text{O}_2\text{S}_2$ 466.1425. Found 466.1425 \pm 0.001.

2,18-Dithia[3.1.3.1]paracyclophane-10-ol (3)

2 g (5.4 mmol) bis(4-bromomethylphenyl)methanol 17 and 1.4 g (5.4 mmol) bis(4-mercaptomethylphenyl)methane 14 were dissolved in 200 ml of a benzene/ethanol mixture 1:1. This solution was given under N_2 -atmosphere to 1.5 l of a solution of 1.3 g of KOH in ethanol during 48 hours. After the end of the reaction the mixture was concentrated in vacuo to 100 ml and hydrolyzed. The water layer was saturated with NaCl and extracted with CH_2Cl_2 . The combined extracts were dried (Na_2SO_4), heated on a water bath, filtered and concentrated to 50 ml. On cooling, 3 separated as colourless crystals. Recrystallization from CH_2Cl_2 gave 1.01 g of 3 (40%), mp 258-259°C. $^1\text{H-NMR}$ (300 MHz) see above. IR (KBr) 3100-3600 (m), 3020 (w), 2920 (w), 2920 (w), 1510 (s), 1420 (s), 1030 (s), 1010 (s), 830 (s) cm^{-1} . MS: m/z (rel. intensity) 468 (M^+ , 25), 450 (100), 225 (31), 195 (49), 193 (51). HRMS calc. for $\text{C}_{30}\text{H}_{28}\text{O}_2\text{S}_2$ 468.1582. Found 468.1581 \pm 0.001.

[2.1.2.1]Paracyclophane (4)

1 g (2.2 mmol) 2,18-dithia[3.1.3.1]paracyclophane was suspended in 500 ml of trimethylphosphite and photolyzed in a photolysis apparatus during 5 hours. At the end of the reaction, most of the solvent was removed, and the reaction mixture was hydrolyzed to destroy the remaining trimethylphosphite. The water layer was extracted with ether; the ether layer was dried over Na_2SO_4 and filtered. The ether was evaporated, and the residue was crystallized from CH_2Cl_2 . 250 mg (29%) colourless crystals, mp 197-199°C. $^1\text{H-NMR}$ (300 MHz) see above. IR (CCl_4) 3000 (w), 2920 (w), 1490 (s), 1420 (m), 1100 (m), 840 (m), 800 (s), 600 (m). MS: m/z (rel. intensity) 388 (M^+ , 100), 143 (87), 179 (26), 164 (34). The spectroscopic data are in good agreement with the data published for 4.³

[2.1.2.1]Paracyclophane-9-one (5)

1 g (2.1 mmol) of 2,18-dithia[3.1.3.1]paracyclophane-10-one (2) was photolyzed within 4 hours by suspending small portions of 2 in 500 ml of trimethylphosphite. After the end of the reaction, most of the solvent was removed, and the remaining part hydrolyzed. The aqueous mixture was repeatedly extracted with ether. The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The residue was crystallized from CH_2Cl_2 . 123 mg colourless crystals (14%), mp 220°C. $^1\text{H-NMR}$ (300 MHz) see above. IR (CCl_4) 3000 (s), 2850 (s), 1670 (m), 1605 (w), 1440 (m), 1380 (s), 810 (s) cm^{-1} . MS : m/z (rel. intensity) 402 (M^+ , 100), 193 (39), 179 (33). HRMS calc. for $\text{C}_{23}\text{H}_{26}\text{O}$ 402.1484. Found 402.1992 \pm 0.001.

[2.1.2.1]Paracyclophane-9-ol (6)

1 g (2.1 mmol) 2,18-dithia[3.1.3.1]paracyclophane-10-ol (3) was suspended in 500 ml of trimethylphosphite and photolyzed at room temperature during 4 hours. Most of the solvent was removed, and the remaining part hydrolyzed. The aqueous layer was saturated with NaCl and extracted with ether. The extracts were dried over Na_2SO_4 , filtered and evaporated. The residue was chromatographed on silica gel with CHCl_3 and crystallized from CH_2Cl_2 . White crystals, 33 mg (4%), mp 196–197°C. $^1\text{H-NMR}$ (300 MHz) see above. IR (CCl_4) 3620 (m), 3010 (m), 2420 (m), 1270 (s), 1440 (m), 1220 (m), 1010 (s), 810 (s). MS : m/z (rel. intensity) 404 (M^+ , 100), 386 (3), 313 (51), 285 (31), 209 (60), 195 (63), 193 (61). HRMS calc. for $\text{C}_{30}\text{H}_{28}\text{O}$ 404.2140. Found 404.2144 \pm 0.001.

[2.1.2.1]Paracyclophane-9,24-dione (7)

500 mg (1.29 mmol) [2.1.2.1]paracyclophane was dissolved in 200 ml dry CCl_4 , and 690 mg (3.9 mmol) N-bromosuccinimide was added. This vigorously stirred mixture was irradiated with a 500 W photolamp in about 30 cm distance keeping the reaction temperature below 40°C. The reaction was finished, when the colour of the reaction mixture had changed from deep brown to yellow. The succinimide was filtered off, and the CCl_4 was evaporated. The residue was dissolved in 100 ml THF, and 100 ml of a saturated K_2CO_3 solution was added. This mixture was refluxed during 10 hours. After cooling, the solution was extracted with four 50 ml portions of ether, dried (Na_2SO_4), and the ether was evaporated. The residue was dissolved in 50 ml of dry CH_2Cl_2 , and 400 mg (1.85 mmol) pyridiniumchlorochromate was added. This mixture was stirred for 2 hours. Then, 100 ml of dry ether was added, the solution was decanted, and the black residue was washed with three 50 ml portions of ether. The combined solutions were filtered over a 5 cm thick layer of silica gel which was washed with ether. The filtrate was evaporated, and the residue was chromatographed on silica gel with CHCl_3 as eluent. The product was crystallized from acetone. 115 mg (22%) colourless product, mp 333–335°C. $^1\text{H-NMR}$ (300 MHz) see above. IR (CCl_4) 3020 (w), 2920 (w), 1660 (s), 1410 (m), 1175 (m), 840 (m) cm^{-1} . MS : m/z (rel. intensity) 416 (M^+ , 97), 388 (7), 208 (28), 180 (100), 165 (32). HRMS calc. for $\text{C}_{30}\text{H}_{24}\text{O}_2$ 416.1776. Found 416.1773 \pm 0.001.

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