

# Double-Layered 1,4-Distyrylbenzene Chromophores – Synthesis, UV and Fluorescence Spectra<sup>☆</sup>

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The reaction of [2.2]paracyclophane (**1**) with liquid bromine affords a 1:1 mixture of only two isomeric products, the *pseudo-para* **2** and *pseudo-ortho* tetrabromide **3**. The structure of the *pseudo-para* isomer **2** has been determined by X-ray structure analysis. Fourfold palladium-catalyzed coupling with styrenes and with methyl acrylate converts **2** and **3** into double-layered derivatives as e.g. **6a**, **7a**, and **7b**, respectively.

The molecular structure of **7a** has been established by X-ray structure analysis. The UV and fluorescence spectra of a variety of substituted products are reported and compared with those of the parent chromophors 2,5-dimethyl-1,4-distyrylbenzene (**16**) and 2,5-diethyl-1,4-bis(phenylethynyl)benzene (**17**), respectively.

The UV and fluorescence spectra of aromatic systems change remarkably with the extent of conjugation. But besides these intramolecular effects intermolecular interactions lead to phenomena such as fluorescence of excimers<sup>[1]</sup> or intense charge-transfer absorptions. The response of a composite chromophore to light is strongly influenced by the relative orientation of its subunits. Chemical bonds between chromophoric subunits can generate composite chromophores of fixed geometry with enhanced charge-transfer interaction. This has been verified inter alios by Staab et al.<sup>[2]</sup> using the [2.2]paracyclophane skeleton to hold two chromophoric units at close distance with a rigid geometry. In view of the strong  $\pi,\pi$ -interaction between the aromatic rings in [2.2]paracyclophane<sup>[3]</sup>, one can think of an electronic coupling between two chromophores "clamped" together at such a distance. As 1,4-distyrylbenzene<sup>[4]</sup> is a well established commercially available laser dye, we have set out to test the spectroscopic properties of [2.2]paracyclophane derivatives containing two 1,4-distyrylbenzene units and similar "double-layered" chromophores.

## Syntheses of New Compounds

A fourfold arene functionalization of [2.2]paracyclophane **1** can be achieved in a single step by the treatment of **1** with liquid bromine and catalytic amounts of iodine<sup>[5]</sup>. Equal amounts of only the two isomeric tetrabromides **2** and **3** are obtained in high yield. Because of their considerably differing solubility in dichloromethane **2** and **3** can easily be separated on a multigram scale. As the two aromatic rings in **1** behave like a single  $\pi$ -system, this transformation corre-

sponds to a perbromination. In addition, further bromination is probably encumbered by steric hindrance.

The constitution of **2** has been verified by X-ray structure analysis (see Figure 1). In the crystal, the two aromatic rings are displaced against each other, causing a torsional angle within the ethano bridge of 14°. All other bond lengths and angles are, as expected, nearly identical with those in the parent compound **1**<sup>[6]</sup>.

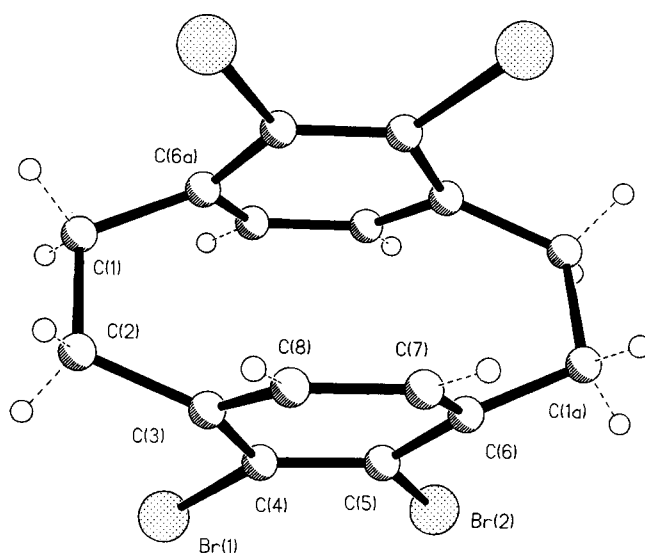
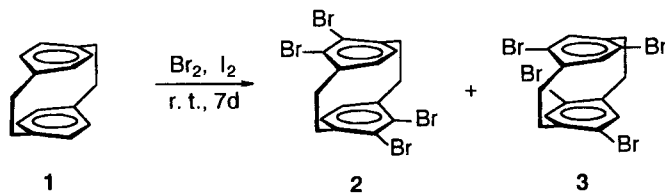
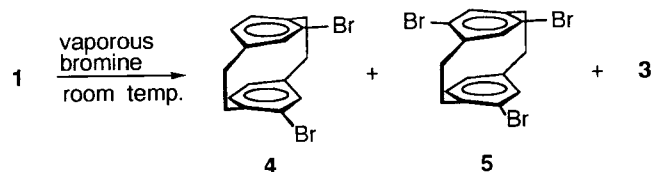


Figure 1. Molecular structure of 4,7,12,15-tetrabromo[2.2]paracyclophane (**2**). Selected bond lengths [pm]: Br(1)—C(4) 189.4(5), C(1)—C(2) 158.8(8), C(2)—C(3) 151.5(6), C(3)—C(8) 139.8(7), C(5)—C(6) 139.3(7), C(7)—C(8) 138.6(6); bond angles [°]: C(1)—C(2)—C(3) 111.9(4), C(2)—C(3)—C(4) 123.3(4), C(4)—C(3)—C(8) 115.8(4), Br(1)—C(4)—C(5) 120.7(3); dihedral angle [°]: C(3)—C(2)—C(1)—C(6a) 14.8; bending of *para*-bridged benzene rings: angle between axis C(2)—C(3) and plane C(4)—C(3)—C(8) 9.8°, angle between plane C(4)—C(3)—C(8) and plane C(4)—C(5)—C(7)—C(8) 14.6°



The *pseudo-para* tetrabromide **2** is formed from **1** only when dissolved in liquid bromine, exposure to bromine vapor leads to a mixture of di- **4**, tri- **5** and tetrabromide **3**, all with *pseudo-ortho* orientation.



The palladium-catalyzed coupling of **3** with alkenes has been performed according to the protocol of Jeffery<sup>[8]</sup>, with a phase-transfer catalyst and a solid base. The fourfold coupling products have been obtained with total yields up to 70%. As four new carbon-carbon bonds are formed in these transformation, each single coupling step must proceed with excellent yield. All these reactions lead stereoselectively to products with (*E*)-configured double bonds.

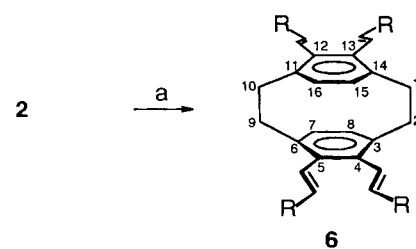
The analogous coupling of 4-bromo[2.2]paracyclophane **8**<sup>[9]</sup>, the dibromide **4** and tribromide **5** gives derivatives with one, two or three styryl or acrylate substituents (**9a**<sup>[10]</sup>, **9b**, **10a,b** and **11a,b**).

Table 1. Palladium-catalyzed coupling reactions of ring brominated [2.2]paracyclophanes with alkenes

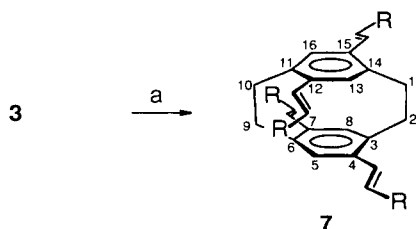
Bromo-arene	Alkene <sup>[a]</sup>	Product	R	Yield (%)
<b>2</b>	styrene	<b>6a</b>	C <sub>6</sub> H <sub>5</sub>	45 <sup>[b]</sup>
<b>3</b>	styrene	<b>7a</b>	C <sub>6</sub> H <sub>5</sub>	70
<b>8</b>	styrene	<b>9a</b>	C <sub>6</sub> H <sub>5</sub>	48 <sup>[b]</sup>
<b>4</b>	styrene	<b>10a</b>	C <sub>6</sub> H <sub>5</sub>	35
<b>5</b>	styrene	<b>11a</b>	C <sub>6</sub> H <sub>5</sub>	37
<b>3</b>	methyl acrylate	<b>7b</b>	CO <sub>2</sub> Me	56
<b>8</b>	methyl acrylate	<b>9b</b>	CO <sub>2</sub> Me	46
<b>4</b>	methyl acrylate	<b>10b</b>	CO <sub>2</sub> Me	40
<b>3</b>	<i>o</i> -methylstyrene	<b>7c</b>	<i>o</i> -Me-C <sub>6</sub> H <sub>4</sub>	41 <sup>[b]</sup>
<b>3</b>	<i>m</i> -methylstyrene	<b>7d</b>	<i>m</i> -Me-C <sub>6</sub> H <sub>4</sub>	30 <sup>[b]</sup>
<b>3</b>	<i>p</i> -methylstyrene	<b>7e</b>	<i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>	44 <sup>[b]</sup>
<b>3</b>	<i>p</i> -methoxystyrene	<b>7f</b>	<i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub>	46 <sup>[b]</sup>
<b>3</b>	methyl <i>p</i> -vinylbenzoate	<b>7g</b>	<i>p</i> -MeO <sub>2</sub> C-C <sub>6</sub> H <sub>4</sub>	7 <sup>[b]</sup>
<b>3</b>	styrene	<b>12a</b>	C <sub>6</sub> H <sub>5</sub>	14 <sup>[b]</sup>
<b>3</b>	1) methyl <i>p</i> -vinylbenzoate	<b>12g</b>	—	— <sup>[c]</sup>
	2) <i>p</i> -methoxy-styrene	<b>13</b>	—	10 <sup>[d]</sup>

<sup>[a]</sup> Olefins were used in excess, yields based on bromoarenes. — <sup>[b]</sup> Yield after recrystallization, yields of the crude coupling products are 10–15% higher. — <sup>[c]</sup> Not isolated. — <sup>[d]</sup> Major product.

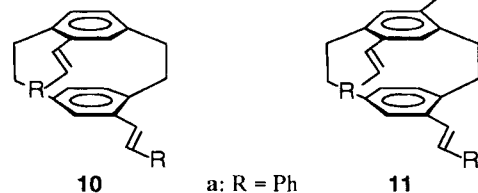
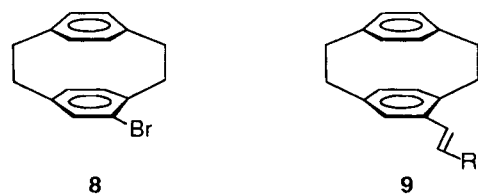
As shown by previous experiments, with *o*- and *p*-dibromoarenes, the second coupling step is accelerated by the vinyl substituents first introduced in the *ortho* or *para* position<sup>[11]</sup>. As a similar effect is not operative for the transannular positions, it is possible to isolate 4,7-bis-coupling products (e.g. **12a**) and also to prepare double-layered compounds of type **13** with two sets of differently substituted



R = see Table 1



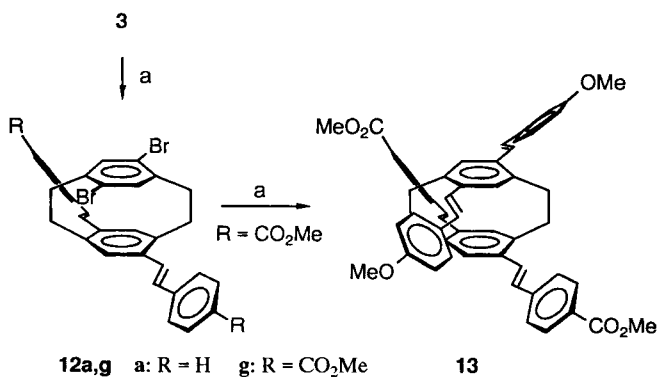
a: Pd(OAc)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, NBu<sub>4</sub>Br, DMF, olefin



a: R = Ph  
b: R = CO<sub>2</sub>Me

styryl groups attached, albeit with low overall yield, without isolating the intermediate bis-coupling products **12**.

The molecular structure of the fourfold styrene adduct **7a** in the crystal has been established by X-ray structure analysis (see Figure 2). The interplanar angles between the phanearene and phenyl moieties vary from 42.3 to 55.8°, presumably caused by intermolecular effects in the crystal.



**12a,g** a: R = H g: R = CO<sub>2</sub>Me

a: Pd(OAc)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, NBu<sub>4</sub>Br, DMF,  $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4\text{OMe}(p)$

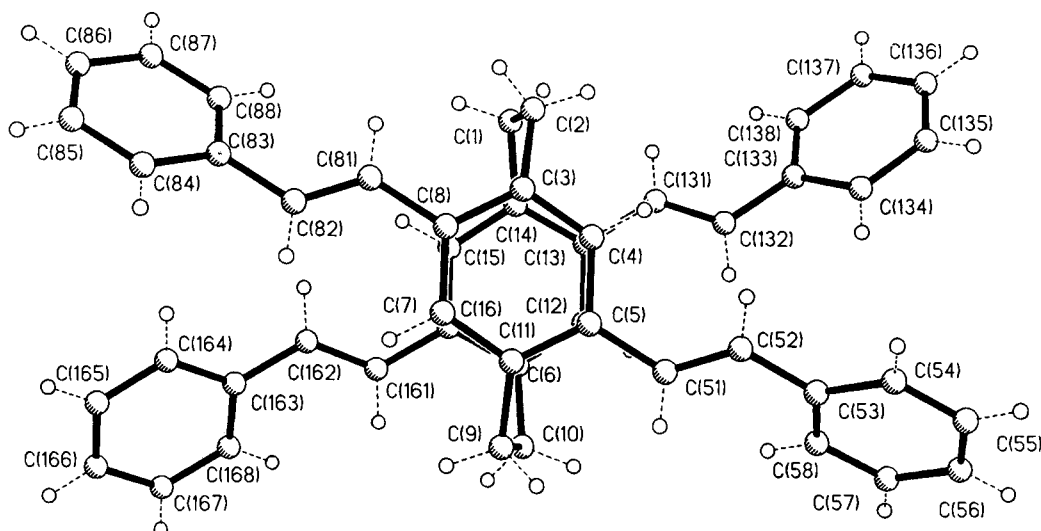
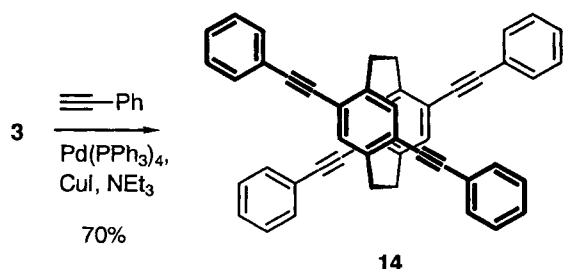


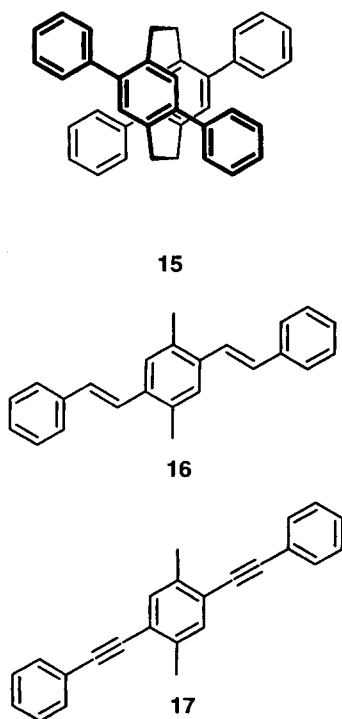
Figure 2. Molecular structure of 4,7,12,15-tetrastyril[2.2]paracyclophane (**7a**). Selected bond lengths [pm]: C(1)–C(2) 158.4(3), C(2)–C(3) 151.8(3), C(3)–C(4) 138.7(4), C(3)–C(8) 140.4(4), C(4)–C(5) 139.9(3), C(8)–C(81) 147.0(4), C(81)–C(82) 131.6(4), C(82)–C(83) 147.3(4); bond angles [°]: C(1)–C(2)–C(3) 111.8(2), C(2)–C(3)–C(8) 123.0(2), C(4)–C(3)–C(8) 117.6(2), C(3)–C(4)–C(5) 123.0(2), C(4)–C(5)–C(51) 120.5(2), C(10)–C(11)–C(16) 122.2(2), C(5)–C(51)–C(52) 127.1(2), C(52)–C(53)–C(54) 121.0(3); dihedral angles [°]: C(3)–C(2)–C(1)–C(14) 22.3, C(4)–C(5)–C(51)–C(52) 26.6, C(5)–C(51)–C(52)–C(53) 9.7, C(51)–C(52)–C(53)–C(54) 22.1; bending of *para*-bridged benzene rings: angle between axis C(2)–C(3) and plane C(4)–C(3)–C(8) 12.5°, angle between plane C(4)–C(3)–C(8) and plane C(4)–C(5)–C(7)–C(8) 12.8°



As the  $D_{2d}$ -symmetric molecules are chiral the investigated racemic crystal contains two enantiomeric molecules in the unit cell, interrelated with each other by a center of symmetry.

With the catalytic system tetrakis(triphenylphosphane)-palladium–copper iodide<sup>[12]</sup>, **3** can be transformed with phenylacetylene to yield the double-layered analog **14** of 1,4-bis(phenylethynyl)benzene.

Nickel-catalyzed coupling of phenylmagnesium bromide with **3** leads to the known *anti*-[2.2](2',5')-*p*-terphenylphane (**15**)<sup>[13]</sup>, albeit in low yield.



### UV/Vis and Fluorescence Spectra

Solutions of the new [2.2]paracyclophane derivatives **11** and **6**, **7** with three and four styrene units attached show intense blue-green fluorescence when exposed to daylight. In comparison with 2,5-dimethyl-1,4-distyrylbenzene (**16**) the UV spectrum of **7a** ( $\lambda_{\text{max}} = 394$  nm) shows a bathochromic shift of 41 nm of the long wavelength absorption band<sup>[14]</sup> and a significant increase in the extinction coefficients. Additional absorptions are observed for **7a** at 278 and 328 nm. Excitation of **7a** at 394, 355 or 339 nm causes a broad, unstructured emission band at 465 nm shifted 61 nm towards longer wavelengths when compared with the corresponding well structured band of **16**. The relative quantum yield  $\Phi$  of **7a** has been determined to be 0.6 (1,4-distyrylbenzene:  $\Phi = 0.78$ <sup>[14]</sup>). It is most likely that the bathochromic shifts of absorption and emission bands of **7a** are caused by the strong electronic interaction between the two 1,4-distyryl chromophors across the central [2.2]paracyclophane, at least to a certain extent<sup>[14]</sup>.

The electronic spectra should be influenced by the torsional angles within the stilbene units, yet the steric influence

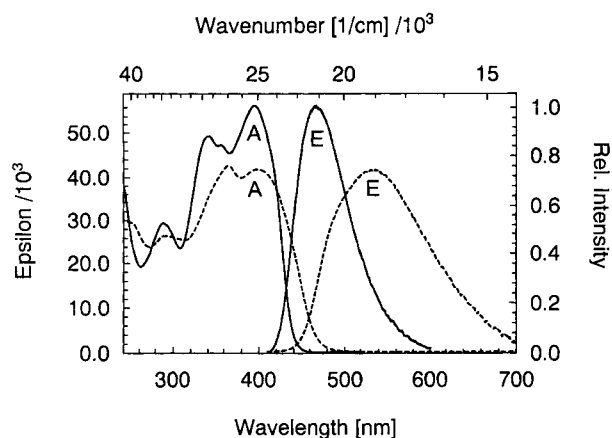


Figure 3. Absorption (A) and emission (E) spectra of **7a** (—, excitation at 394 nm), and **13** (---, excitation at 399 nm) in dichloromethane

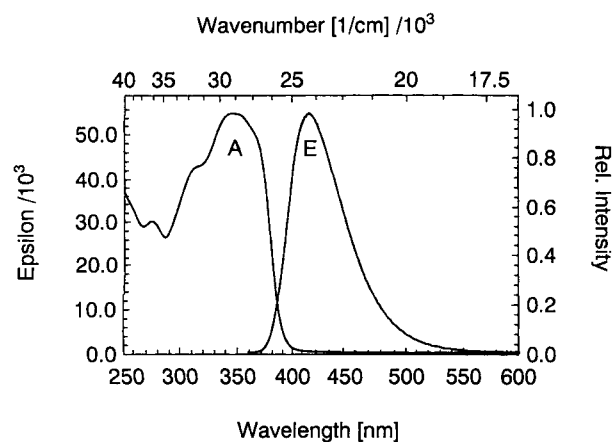


Figure 4. Absorption (A) and emission (E) spectra of **14**, excitation at 346 nm in dichloromethane

of methyl substituents in the 2-, 3- or 4-position of the phenyl rings as in **7c**, **7d** and **7e** is too small to cause any change in the absorption spectra ( $\lambda_{\max} = 394$ , 395, and 397 nm, respectively).

Methoxy or methoxycarbonyl substituents in the *para*-position of all styryl groups cause small shifts in the absorption (+8 and -4 nm) and emission (+9 and +19 nm) spectra of **7f** and **7g** with respect to **7a**. With electron-donating substituents in one and attracting groups in the other 1,4-distyryl chromophore as in **13**, a very broad (band half width  $4570 \text{ cm}^{-1}$ ) and bathochromically shifted band ( $\lambda_{\max} = 534 \text{ nm}$ ) is observed. The large Stokes shift of  $6340 \text{ cm}^{-1}$  as compared to  $3880 \text{ cm}^{-1}$  in **7a** (band half width  $3100 \text{ cm}^{-1}$ ) suggests that the fluorescence of **13** originates from an excimer rather than a charge-transfer complex.

A comparison of the emission spectra (see Experimental) of **9**, **10** and **11** reveals that each additional styryl group causes a bathochromic shift of the emission maximum by 20 nm.

**7b** and **7a** have similar emission bands, although the relative quantum yield  $\Phi$  of **7b** is only 0.2. The absorption spectrum of **7b** shows shorter wavelength bands. Replacing

the ethenyl subunits in **7a** by ethynyl as in tetrakis(*p*-phenylethynyl)[2.2]paracyclophane (**14**) hypsochromically shifts both the absorption ( $\lambda_{\max} = 346 \text{ nm}$ ) and the emission band (415 nm) by approx. 50 nm without a significant change in the extinction coefficient of the longest wavelength absorption. In contrast to compounds **7a** and **16**, 2,5-dimethyl-1,4-bis(phenylethynyl)benzene (**17**), the parent chromophore to **14**, shows a hypsochromic shift of the emission band (353 nm) by 62 nm with a much smaller shift (18 nm) of the long wavelength absorption ( $\lambda_{\max} = 328 \text{ nm}$ ) leading to a Stokes shift of only  $2220 \text{ cm}^{-1}$ . Its increase to  $4810 \text{ cm}^{-1}$  on going to the double-layered **14** again may be attributed to fluorescence arising from an excimer.

**7a** and **14** were tested for laser application, but a stimulated emission has not been observed in both cases<sup>[15]</sup>.

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## Experimental

<sup>1</sup>H NMR: Bruker WM 250;  $\delta = 0$  for tetramethylsilane as internal standard,  $\delta = 7.26$  for chloroform. — <sup>13</sup>C NMR: Bruker WM 250;  $\delta = 77$  for deuteriochloroform; assignments were aided by the measurement of DEPT spectra, + designates primary and tertiary, - secondary and C<sub>quat</sub> quaternary carbon atoms. — IR: Perkin-Elmer 297 and 399. — MS: Varian MAT CH7 (70 eV) and VG-70-250S (VG Analytical). — UV/Vis: Cary 219 (Varian). — Fluorescence: Perkin-Elmer MPF-44A. — Melting points were determined with an Electrothermal melting point apparatus and are uncorrected. — Column chromatography (CC): Merck silica gel 60, mesh 70–230; PE (60/70) means petroleum ether with a boiling range of 60–70 °C. — TLC was carried out on silica gel (Merck F<sub>254</sub>).

*X-ray Crystal Structure Analyses of 2 and 7a*: Intensity data were measured with a STOE AED2, Version 6.2 diffractometer, by using graphite-monochromated Mo-*K*<sub>α</sub> radiation ( $\lambda = 71.069 \text{ pm}$ ,  $\Theta/2\Theta$  scanning technique). Selected bond lengths and angles of structure **2** are given in Figure 1, for structure **7a** in Figure 2. Final fractional

Table 2. Fractional atomic coordinates [ $\times 10^4$ ] and equivalent isotropic thermal parameters [ $\text{pm}^2 \times 10^{-1}$ ] for non-hydrogen atoms of 4,7,12,15-tetrabromo[2.2]paracyclophane (**2**) with e.s. d.'s of the least significant figure in parentheses; equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor

	x	y	z	<i>U</i> (eq)
Br(1)	7642(1)	1750(1)	6971(1)	47(1)
Br(2)	5437(1)	917(1)	2914(1)	41(1)
C(1)	12589(7)	1092(4)	7989(6)	34(2)
C(2)	11352(7)	400(4)	8777(6)	38(2)
C(3)	9756(6)	-116(4)	7348(6)	28(2)
C(4)	8248(6)	440(4)	6219(6)	28(2)
C(5)	7290(6)	71(4)	4526(6)	25(2)
C(6)	7777(6)	-867(3)	3925(6)	25(2)
C(7)	8944(6)	-1520(4)	5203(6)	28(2)
C(8)	9906(7)	-1158(4)	6884(6)	29(2)

atomic coordinates and equivalent isotropic thermal parameters [ $\text{pm}^3$ ] for non-hydrogen atoms are given in Tables 2 and 3.

4,7,12,15-Tetrabromo[2.2]paracyclophane (**2**):  $\text{C}_{16}\text{H}_{12}\text{Br}_4$ , 523.9 g  $\text{mol}^{-1}$ , monoclinic crystals, space group  $P2_1/n$ ,  $Z = 2$ , unit cell dimensions  $a = 769.7(1)$ ,  $b = 1276.9(3)$ ,  $c = 812.1(1)$  pm,  $\beta = 110.41(1)^\circ$ ,

Table 3. Fractional atomic coordinates [ $\times 10^4$ ] and equivalent isotropic thermal parameters [ $\text{pm}^2 \times 10^{-1}$ ] for non-hydrogen atoms of 4,7,12,15-tetrastyril[2.2]paracyclophane (**7a**) with e.s. d.'s of the least significant figure in parentheses; equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

	x	y	z	$U(\text{eq})$
C(1)	-629(3)	6736(2)	9175(2)	63(1)
C(2)	-425(2)	8110(2)	9007(2)	61(1)
C(3)	1134(3)	8677(2)	9342(2)	54(1)
C(4)	2165(3)	8857(2)	8826(2)	56(1)
C(5)	3703(3)	8855(2)	9068(2)	53(1)
C(6)	4204(2)	8680(2)	9881(2)	53(1)
C(7)	3216(3)	8776(2)	10409(2)	53(1)
C(8)	1677(3)	8776(2)	10160(2)	53(1)
C(9)	5652(2)	8159(2)	10179(2)	57(1)
C(10)	5563(3)	6807(2)	9935(2)	59(1)
C(11)	3962(3)	6245(2)	9747(2)	52(1)
C(12)	3271(3)	6133(2)	8962(2)	56(1)
C(13)	1725(3)	6109(2)	8727(2)	57(1)
C(14)	853(3)	6222(2)	9327(2)	56(1)
C(15)	1510(3)	6069(2)	10107(2)	56(1)
C(16)	3046(3)	6066(2)	10334(2)	52(1)
C(51)	4709(3)	8824(2)	8480(2)	59(1)
C(52)	4497(3)	9213(2)	7750(2)	71(1)
C(53)	5403(3)	9018(3)	7132(2)	76(1)
C(54)	5425(4)	9765(3)	6495(2)	106(2)
C(55)	6231(5)	9549(5)	5900(2)	132(2)
C(56)	7014(5)	8604(5)	5925(3)	138(3)
C(57)	6995(4)	7862(4)	6539(3)	126(2)
C(58)	6214(4)	8062(3)	7140(2)	95(1)
C(81)	645(3)	8675(4)	10743(2)	57(1)
C(82)	981(3)	8911(2)	11510(2)	66(1)
C(83)	-51(3)	8743(3)	12094(2)	72(1)
C(84)	187(4)	9416(3)	12782(2)	96(2)
C(85)	-783(7)	9277(4)	13323(3)	131(2)
C(86)	-1998(6)	8457(6)	13188(3)	151(3)
C(87)	-2240(5)	7790(5)	12515(3)	149(3)
C(88)	-1289(4)	7920(3)	11976(2)	106(2)
C(131)	1047(3)	6117(2)	7886(2)	67(1)
C(132)	1702(3)	6526(2)	7285(2)	72(1)
C(133)	962(3)	6564(3)	6456(2)	75(1)
C(134)	1503(4)	7393(3)	5950(2)	98(2)
C(135)	766(5)	7481(4)	5186(2)	114(2)
C(136)	-486(5)	6745(4)	4907(2)	117(2)
C(137)	-1013(4)	5903(3)	5390(2)	105(2)
C(138)	-307(3)	5810(3)	6153(2)	85(1)
C(161)	3698(3)	6012(2)	11177(2)	59(1)
C(162)	3052(3)	6237(2)	11799(2)	68(1)
C(163)	3700(3)	6159(2)	12642(2)	66(1)
C(164)	3218(4)	6822(3)	13209(2)	100(2)
C(165)	3872(5)	6810(3)	13994(2)	115(2)
C(166)	4980(4)	6125(3)	14228(2)	101(2)
C(167)	5445(3)	5444(3)	13684(2)	100(2)
C(168)	4810(3)	5456(3)	12900(2)	83(1)

$V = 748.0(2) \cdot 10^6 \text{ pm}^3$ ,  $Q_{\text{calcd.}} = 2.33 \text{ g cm}^{-3}$ , 2348 observed reflections with  $2\Theta < 45^\circ$ ,  $\text{MoK}\alpha$ ,  $R_w = 3.73\%$ <sup>[7]</sup>.

4,7,12,15-Tetrastyril[2.2]paracyclophane (**7a**):  $\text{C}_{48}\text{H}_{40}$ , 616.8 g  $\text{mol}^{-1}$ , triclinic crystals, space group  $P1$ ,  $Z = 2$ , unit cell dimensions  $a = 912.2(1)$ ,  $b = 1135.9(1)$ ,  $c = 1705.0(2)$  pm,  $\alpha = 90.27(1)$ ,  $\beta = 99.09(1)$ ,  $\gamma = 96.30(1)^\circ$ ,  $V = 1733.5(3) \cdot 10^6 \text{ pm}^3$ ,  $Q_{\text{calcd.}} = 1.182 \text{ mg cm}^{-3}$ , 3419 observed reflections with  $2\Theta < 45^\circ$ ,  $\text{MoK}\alpha$ ,  $R_w = 5.74\%$ <sup>[7]</sup>.

4,7,12,15- and 4,5,12,13-Tetrabromo[2.2]paracyclophane (**2** and **3**): 10.0 g (48 mmol) of [2.2]paracyclophane (**1**) is slowly added in small portions to a mixture of 30 ml (589 mmol, 94.2 g) of bromine and 150 mg (0.6 mmol) of iodine. The solution is kept in the dark (vigorous evolution of hydrogen bromide!) and stirred for 8 d at room temp. in a flask wrapped with aluminum foil to exclude daylight. The reaction mixture is then decomposed by addition of 300 ml of 20% aqueous sodium hydroxide. The precipitate is collected by filtration, washed with  $3 \times 50$  ml of hot ethanol and dried in vacuo, yield 23.8 g (91%) as a mixture of **2** and **3** in equal amounts. To separate the isomers the product mixture is extracted with  $4 \times 80$  ml of dichloromethane yielding a residue of 11.2 g (43%) of almost pure **2**. A small sample was recrystallized from toluene for analytical characterization affording bright, cubic crystals, m.p.  $> 280^\circ\text{C}$ . — IR (KBr):  $\tilde{\nu} = 2936 \text{ cm}^{-1}$ , 1439, 1064, 839. —  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 3.10$  and  $3.38$  [m, 8H, 1(2,9,10)-H], 7.00 (s, 4H, phane-arene-H). —  $^{13}\text{C NMR}$  (62.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 34.6$  [–, C-1(2,9,10)], 128.7 (+, C-phane-arene), 129.3 and 140.7 ( $\text{C}_{\text{quat}}$ ). — MS (70 eV):  $m/z$  (%) = 528/526/524/522/520 (4/12/22/12/1) [ $\text{M}^+$ ], 264/262/260 (44/100/44) [ $\text{M}^{2+}$ ]. —  $\text{C}_{16}\text{H}_{12}\text{Br}_4$  (523.9): calcd. C 36.68, H 2.31, Br 61.01; found C 36.48, H 2.29, Br 61.13.

The dichloromethane filtrate is evaporated to dryness to yield 12.4 g (40%) of a 85:15 mixture of **2** and **3** (according to  $^1\text{H NMR}$ ). A pure sample of **3** is obtained by chromatography of 1 g of the mixture over 100 g of silica gel [PE (60/70)] ( $R_f = 0.33$ ), white solid, m.p.  $> 280^\circ\text{C}$ . —  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 3.00$ – $3.50$  [m, 8H, 1(2,9,10)-H], 7.28 (s, 4H, phane-arene-H). —  $^{13}\text{C NMR}$  (62.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 32.5$  [–, C-1(2,9,10)], 134.5 (+, C-phane-arene), 140.4 ( $\text{C}_{\text{quat}}$ ).

Reaction of **1** with Vaporous Bromine: 3.0 g (14.4 mmol) of **1**, finely powdered in a crystallization beaker (10 cm), is kept in the dark in a desiccator (15 cm) with 9.23 g (2.9 ml, 58 mmol) of bromine. The orange solid obtained is subjected to CC over 200 g of silica gel [PE (60/70)] to yield fraction I ( $R_f = 0.55$ ): 432 mg (8.2%) of 4,12-dibromo[2.2]paracyclophane (**4**)<sup>[9]</sup>. —  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.80$ – $3.60$  [m, 8H, 1(2,9,10)-H], 6.48 (m, 4H), 7.18 (m, 2H). —  $^{13}\text{C NMR}$  (62.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 32.8$  and  $35.4$  [–, C-1(2,9,10)], 126.7 ( $\text{C}_{\text{quat}}$ ), 128.3, 134.1 and 137.3 (+), 138.5 and 141.2 ( $\text{C}_{\text{quat}}$ ). — MS (70 eV):  $m/z$  (%) = 368/366/364 (18/38/18) [ $\text{M}^+$ ], 184/182 (96/100). — II ( $R_f = 0.42$ ): 1.9 g (30%) of 4,7,12(15)-tribromo[2.2]paracyclophane (**5**), m.p.  $> 280^\circ\text{C}$ . —  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.82$ – $3.31$  [m, 8H, 1(2,9,10)-H], 6.40– $7.38$  (m, 5H). —  $^{13}\text{C NMR}$  (62.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 32.3$ , 32.8, 33.1, 33.3, 34.5, 35.1, and 36.8 (–), 124.97, 125.01, and 126.4 ( $\text{C}_{\text{quat}}$ ), 127.8, 128.6, 129.1, 129.5, 130.9, 131.0, 132.0, 133.8, 136.5, 137.0, and 138.2 (+), 138.4, 140.6, 140.7, and 140.8 ( $\text{C}_{\text{quat}}$ ). — MS (70 eV):  $m/z$  (%) = 448/446/444/442 (6/20/20/6) [ $\text{M}^+$ ], 184/182 (96/100). — III ( $R_f = 0.33$ ): 1.2 g (15.3%) of **2**.

General Procedure (GP) for the Palladium-Catalysed Coupling of Bromo[2.2]paracyclophanes (GP 1): A mixture of 1.0 mmol of **2** or **3**, 10.0 mmol of potassium carbonate ( $\text{K}_2\text{CO}_3$ ), 4.0 mmol of tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ), the given amount of the appropriate alkene and 25 mg (0.11 mmol) of palladium acetate [ $\text{Pd}(\text{OAc})_2$ ] in 20 ml of dimethylformamide (DMF) is heated in a

capped pyrex tube under nitrogen for the time stated. The reaction mixture is diluted with 100 ml of dichloromethane, filtered and the filtrate washed with eight portions of 50 ml of water. The combined aqueous layers are reextracted with 50 ml of dichloromethane, the collected organic phases are dried with magnesium sulfate (MgSO<sub>4</sub>), filtered and the solvent is evaporated in vacuo. Chromatography of the crude products over silica gel and subsequent recrystallization afford the pure compounds.

**4,5,12,13-Tetrastyril[2.2]paracyclophane (6a):** 400 mg (0.76 mmol) of **2** and 2.0 ml (17.5 mmol) of styrene are allowed to react for 3 d at 100 °C according to GP 1. CC over 50 g of silica gel [dichloromethane/PE (60/70), 7:3, R<sub>f</sub> = 0.31] yields 211 mg of **6a** (45%), yellow solid, m.p. 218 °C. — <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.8–3.7 [m, 8H, 1(2,9,10)-H], 6.7 and 7.0–7.6 (m, 32H). — <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>): δ = 31.4, 32.8, 33.7, and 34.8 [–, C-1(2,9,10)], 126.3, 126.6, 127.6, 127.6, 128.8, 134.8, 135.0, and 135.2 (+), 137.3, 137.9, and 139.5 (C<sub>quat</sub>). — MS (70 eV): m/z (%) = 616 (3.7) [M<sup>+</sup>], 307 (100). — C<sub>48</sub>H<sub>40</sub> (256.8): calcd. C 93.51, H 6.49; found C 93.25, H 6.48; C 93.46, H 6.61.

**4,7,12,15-Tetrastyril[2.2]paracyclophane (7a):** 1.05 g (2.0 mmol) of **3** is treated with 5.0 ml (44 mmol) of styrene for 2 d at 100 °C according to GP 1. CC of the crude product over 100 g of silica gel [dichloromethane/PE (60/70), 1:1] yields 860 mg (70%) of **7a** (R<sub>f</sub> = 0.51). After recrystallization from heptane/toluene (1:1) 604 mg (49%) of **7a** is obtained as a bright yellow solid, m.p. 232 °C. — IR (KBr): ν̄ = 2927 cm<sup>-1</sup>, 1495, 956, 754, 691. — UV (dichloromethane): λ<sub>max</sub> (lg ε) = 238 nm (4.578), 286 (4.466), 339 (4.690), 355 (4.671), 394 (4.747). — Fluorescence (dichloromethane, excitation at 354 nm): λ<sub>max</sub> (rel. intensity) = 465 nm (1.0); Φ<sub>rel</sub> = 0.6. — <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.90 and 3.59 [m, 8H, 1(2,9,10)-H], 6.94 (d, <sup>3</sup>J = 16.0 Hz, 4H, 2'-H), 7.02 (s, 4H, phane-arene-H), 7.24 (d, <sup>3</sup>J = 6.0 Hz, 4H, 1'-H), 7.26–7.52 (m, 20H, phenyl-H). — <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>): δ = 33.1 [–, C-1(2,9,10)], 125.3, 126.6, 127.6, 128.1, and 128.7 (+), 136.7, 137.7, 137.9 (C<sub>quat</sub>). — MS (70 eV): m/z (%) = 616 (10) [M<sup>+</sup>], 307 (100). — C<sub>48</sub>H<sub>40</sub> (256.8): calcd. C 93.51, H 6.49; found C 93.37, H 6.50; C 93.66, H 6.47.

**Tetramethyl[2.2]paracyclophane-4,7,12,15-tetraacrylate (7b):** 5.5 g (10.5 mmol) of **3** and 8.75 g (8.5 ml, 96 mmol) of methyl acrylate are allowed to react according to GP 1 for 3 d at 60 °C. The reaction is initiated by sonification for 1 h. CC over 300 g of silica gel (dichloromethane, R<sub>f</sub> = 0.2) affords 3.2 g of **7b** (56%). Recrystallization from toluene yields 2.75 g (48%) of **7b** as a yellow solid, m.p. 205 °C. — IR (KBr): ν̄ = 2951 cm<sup>-1</sup>, 1713 (s, C=O), 1626 (s), 1328 (s), 1198. — UV (dichloromethane): λ<sub>max</sub> (lg ε) = 227 nm (4.389), 273 (4.479), 355 (4.572). — Fluorescence (dichloromethane, excitation at 355 nm): λ<sub>max</sub> (rel. intensity) = 465 nm (1.0); Φ<sub>rel</sub> = 0.2. — <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.85 and 3.60 [m, 8H, 1(2,9,10)-H], 3.88 (s, 12H, OCH<sub>3</sub>), 6.28 (d, <sup>3</sup>J = 18 Hz, 4H, olefin-H), 6.85 (s, 4H, phane-arene-H), 7.72 (d, <sup>3</sup>J = 18 Hz, 4H, olefin-H). — <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>): δ = 32.9 [–, C-1(2,9,10)], 51.9 (+, OCH<sub>3</sub>), 119.2, 130.3 (+), 136.3 (C<sub>quat</sub>), 140.1 (+), 167.3 (C<sub>quat</sub>, C=O). — MS (70 eV): m/z (%) = 544 (19) [M<sup>+</sup>], 153 (100). — C<sub>32</sub>H<sub>32</sub>O<sub>8</sub> (544.6): calcd. C 70.58, H 5.92; found C 70.70, H 5.95.

**4,7,12,15-Tetra(o-methylstyryl)[2.2]paracyclophane (7c):** 1.0 g (1.9 mmol) of **3** and 4.0 ml (34 mmol) of o-methylstyrene are allowed to react for 2 d at 100 °C according to GP 1. CC over 100 g of silica gel [dichloromethane/PE (60/70), 1:1, R<sub>f</sub> = 0.38] and recrystallization from heptane/toluene (1:1) yield 520 mg of **7c** (41%), yellow crystals, m.p. 185 °C. — IR (KBr): ν̄ = 2950 cm<sup>-1</sup>, 1600, 960. — UV (dichloromethane): λ<sub>max</sub> (lg ε) = 238 nm (4.553), 285 (4.467), 338 (4.658), 352 (4.652), 394 (4.725). — Fluorescence (dichloromethane, excitation at 394 nm): λ<sub>max</sub> (rel. intensity) = 466 nm (1.0); Φ<sub>rel</sub> = 0.45.

— <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.10 (s, 12H, CH<sub>3</sub>), 2.95 and 3.60 [m, 8H, 1(2,9,10)-H], 7.00 (s, 4H, phane-arene-H), 7.10–7.30 and 7.70 (m, 24H, olefin- and phenyl-H). — <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>): δ = 19.8 (+, CH<sub>3</sub>), 33.1 [–, C-1(2,9,10)], 125.3, 126.2, 126.8, 127.0, 127.5, 128.9, 130.5 (+), 136.1, 136.8, 137.3, and 137.9 (C<sub>quat</sub>). — MS (70 eV): m/z (%) = 672 (60) [M<sup>+</sup>], 336 (92), 335 (100). — C<sub>52</sub>H<sub>48</sub> (673.0): calcd. C 92.86, H 7.14; found C 92.88, H 7.13; C 92.87, H 7.15.

**4,7,12,15-Tetra(m-methylstyryl)[2.2]paracyclophane (7d):** 1.0 g (1.9 mmol) of **3** is treated with 5.0 ml (42 mmol) of m-methylstyrene for 2 d at 100 °C according to GP 1 and the crude product obtained is subjected to CC over 100 g of silica gel [dichloromethane/PE (60/70) 1:1, R<sub>f</sub> = 0.35]. Recrystallization from toluene/heptane (1:1) yields 380 mg of **7d** (30%), yellow crystals, m.p. 192 °C. — IR (KBr): ν̄ = 3020 cm<sup>-1</sup>, 2922, 1600, 779. — UV (dichloromethane): λ<sub>max</sub> (lg ε) = 239 nm (4.599), 292 (4.521), 337 (4.724), 395 (4.717). — <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 2.28 (s, 3H, CH<sub>3</sub>), 2.33 (s, 9H, CH<sub>3</sub>), 2.81 and 3.52 [m, 8H, 1(2,9,10)-H], 6.80–7.30 (m, 28H). — <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.5 (+, CH<sub>3</sub>), 33.1 [–, C-1(2,9,10)], 123.5, 123.6, 125.1, 126.5, 127.6, 128.1, 128.4, 128.6, 128.8, 130.1 (+), 136.7, 137.7, 137.8, 138.3 (C<sub>quat</sub>). — MS (70 eV): m/z (%) = 672 (96) [M<sup>+</sup>], 336 (100). — C<sub>52</sub>H<sub>48</sub> (673.0): calcd. C 92.86, H 7.14; found C 92.87, H 7.27.

**4,7,12,15-Tetra(p-methylstyryl)[2.2]paracyclophane (7e):** 1.0 g (1.9 mmol) of **3** and 4.0 ml (34 mmol) of p-methylstyrene are allowed to react for 2 d at 100 °C according to GP 1. CC of the crude product over 100 g of silica gel [dichloromethane/PE (60/70), 1:1, R<sub>f</sub> = 0.40] and recrystallization from heptane/toluene (1:1) afford 562 mg of **7e** (44%), yellow crystals, m.p. 188 °C. — IR (KBr): ν̄ = 3022 cm<sup>-1</sup>, 2922, 1513, 959. — UV (dichloromethane): λ<sub>max</sub> (lg ε) = 241 nm (4.558), 288 (4.445), 342 (4.701), 397 (4.762). — <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.41 (s, 12H, CH<sub>3</sub>), 2.90 and 3.60 [m, 8H, 1(2,9,10)-H], 6.85–7.45 (m, 28H). — <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>): δ = 21.3 (+, CH<sub>3</sub>), 33.1 [–, C-1(2,9,10)], 124.5, 126.6, 127.9, 128.2, and 129.0 (+), 135.0, 136.6, 137.5, and 137.7 (C<sub>quat</sub>). — MS (70 eV): m/z (%) = 672 (90) [M<sup>+</sup>], 335 (100). — C<sub>52</sub>H<sub>48</sub> (673.0): calcd. C 92.86, H 7.14; found C 92.78, H 7.17.

**4,7,12,15-Tetra(p-methoxystyryl)[2.2]paracyclophane (7f):** 1.05 g (2.0 mmol) of **3** and 4.83 g (36.0 mmol) of p-methoxystyrene<sup>[16]</sup> are allowed to react according to GP 1 for 4 d at 80 °C. Chromatography over 100 g of silica gel [dichloromethane/PE (60/70), 1:1, R<sub>f</sub> = 0.25] and recrystallization from heptane/toluene (5:4) yields 670 mg of **7f** (46%), yellow crystals, m.p. 250 °C (dec.). — IR (KBr): ν̄ = 3030 cm<sup>-1</sup>, 2930, 2845, 1610, 1515, 1460, 1250, 1180, 1040, 840. — UV (dichloromethane): λ<sub>max</sub> (lg ε) = 228 nm (4.565), 294 (4.481), 355 (4.739), 402 (4.795). — Fluorescence (dichloromethane, excitation at 402 nm): λ<sub>max</sub> (rel. intensity) = 474 nm (1.0); Φ<sub>rel</sub> = 0.65. — <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.90 and 3.55 [m, 8H, 1(2,9,10)-H], 3.90 (s, 12H, OCH<sub>3</sub>), 6.85–7.50 (m, 28H). — <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>): δ = 33.1 [–, C-1(2,9,10)], 55.4 (+, OCH<sub>3</sub>), 114.2, 123.5, 127.8, and 128.0 (+), 130.6, 136.6, 137.5, and 159.3 (C<sub>quat</sub>). — MS (70 eV): m/z (%) = 736 (0.3) [M<sup>+</sup>], 368 (10) [M<sup>2+</sup>], 122 (100). — C<sub>52</sub>H<sub>48</sub>O<sub>4</sub> (737.0): calcd. C 84.75, H 6.57; found C 84.62, H 6.60.

**4,7,12,15-Tetra(p-methoxycarbonylstyryl)[2.2]paracyclophane (7g):** 1.0 g (1.9 mmol) of **3** and 3.7 g (23 mmol) of methyl p-vinylbenzoate are allowed to react according to GP 1 at 70 °C for 3 d. CC over 100 g of silica gel (dichloromethane) affords two fractions. I (R<sub>f</sub> = 0.9): 1.4 g of methyl p-vinylbenzoate. — II (R<sub>f</sub> = 0.35): 110 mg of **7g** (7%), yellow solid, m.p. 308 °C (dec.). — UV (dichloromethane): λ<sub>max</sub> (lg ε) = 247 nm (4.533), 287 (4.395), 390 (4.613). — Fluorescence (dichloromethane, excitation at 390 nm): λ<sub>max</sub> (rel. intensity) = 468 nm (1.0), 484 (0.99); Φ<sub>rel</sub> = 0.5. — <sup>1</sup>H NMR (250 MHz,

$\text{CDCl}_3$ ):  $\delta = 2.80$  and  $3.50$  (m, 8H),  $3.95$  (s, 12H,  $\text{OCH}_3$ ),  $6.2$ – $7.5$  and  $8.05$  (m, 28H).

**4-Styryl[2.2]paracyclophane<sup>101</sup> (9a)**: 1.0 g (3.5 mmol) of 4-bromo[2.2]paracyclophane<sup>91</sup>, 3.5 ml (30.5 mmol) of styrene, 1.4 g (10 mmol) of  $\text{K}_2\text{CO}_3$ , 1.2 g (3.7 mmol) of  $\text{Bu}_4\text{NBr}$  and 25 mg (0.11 mmol) of palladium acetate are allowed to react under nitrogen in 20 ml of dry DMF for 2 d at  $100^\circ\text{C}$ . Work-up as described in GP 1 and CC of the crude reaction product over 80 g of silica gel [dichloromethane/PE (60/70), 2:8,  $R_f = 0.14$ ] yield 521 mg (48%) of **9a**, white solid, m.p.  $132^\circ\text{C}$ . — UV (dichloromethane):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ) = 228 nm (4.341), 320 (4.312), 395 (1.964). — Fluorescence (dichloromethane, excitation at 320 nm):  $\lambda_{\text{max}}$  (rel. intensity) = 395 nm (1.0);  $\Phi_{\text{rel}} = 0.07$ . —  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 3.00$  and  $3.60$  [m, 8H, 1(2,9,10)-H],  $6.40$ – $7.60$  (m, 14H). —  $^{13}\text{C NMR}$  (62.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 34.0, 34.9, 35.2, \text{ and } 35.5$  [–, C-1(2,9,10)], 126.5, 126.9, 127.5, 128.7, 129.2, 129.8, 130.2, 131.7, 131.8, 133.0, and 134.9 (+), 137.4, 137.9, 138.4, 139.25, 139.31, and 139.9 ( $\text{C}_{\text{quat}}$ ). — MS (70 eV):  $m/z$  (%) = 310 (40) [ $\text{M}^+$ ], 205 (100). —  $\text{C}_{24}\text{H}_{22}$  (310.4): calcd. C 92.90, H 7.10; found C 93.26, H 7.15; C 93.07, H 7.19.

**Methyl 3-(4-[2.2]Paracyclophanyl)acrylate (9b)**: 860 mg (3.0 mmol) of 4-bromo[2.2]paracyclophane<sup>91</sup>, 1.55 g (1.5 ml, 17 mmol) of methyl acrylate, 1.4 g (10 mmol) of  $\text{K}_2\text{CO}_3$ , 1.2 g (3.7 mmol) of  $\text{Bu}_4\text{NBr}$  and 25 mg (0.11 mmol) of palladium acetate are allowed to react under nitrogen in 20 ml of dry DMF for 3 d at  $80^\circ\text{C}$ . Appropriate work-up as described in GP 1 and CC over 80 g of silica gel (dichloromethane) yield 400 mg (46%) of **9b** ( $R_f = 0.38$ ), after recrystallization from toluene/heptane (1:1) 310 mg (35%) of pure **9b**, small white plates, m.p.  $112^\circ\text{C}$ . — IR (KBr):  $\tilde{\nu} = 2998 \text{ cm}^{-1}$ , 1717 (C=O), 980. —  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.8$ – $3.2$  [m, 7H, 1(9,10)-H + 2- $\text{H}_{\text{anti}}$ ], 3.55 (m, 1H, 2- $\text{H}_{\text{syn}}$ ), 3.83 (s, 3H,  $\text{OCH}_3$ ), 6.25 (d,  $^3J = 16.0$  Hz, 1H, 1'-H), 6.4–6.7 (m, 7H, arene-H), 7.80 (d,  $^3J = 16.0$  Hz, 1H, 2'-H). —  $^{13}\text{C NMR}$  (62.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 33.7, 35.0, 35.1, 35.4$  [–, C-1(2,9,10)], 51.7 (+,  $\text{OCH}_3$ ), 117.7 (+, C-1'), 130.5, 131.2, 131.8, 133.0, 133.1, 134.5, 135.2 (+, C-phane-arene), 139.2, 139.3, 140.3, 140.7 ( $\text{C}_{\text{quat}}$ , C-phane-arene), 142.6 (+, C-2'), 167.8 ( $\text{C}_{\text{quat}}$ , C=O). — MS (70 eV):  $m/z$  (%) = 292 (20) [ $\text{M}^+$ ], 104 (100). —  $\text{C}_{20}\text{H}_{20}\text{O}_2$  (292.4): calcd. C 82.19, H 6.85; found C 81.98, H 6.83.

**4,12-Distyryl[2.2]paracyclophane (10a)**: 900 mg (2.46 mmol) of **4** and 3.5 ml (30.5 mmol) of styrene are allowed to react for 2 d at  $100^\circ\text{C}$  according to GP 1. CC over 80 g of silica gel [dichloromethane/PE (60/70), 3:1,  $R_f = 0.6$ ] yields 350 mg (35%) of **10a**, after recrystallization from heptane 255 mg (25%) of **10a**, m.p.  $230^\circ\text{C}$  (dec.). — UV (dichloromethane):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ) = 228 nm (4.396), 310 (4.622). — Fluorescence (dichloromethane, excitation at 310 nm):  $\lambda_{\text{max}}$  (rel. intensity) = 422 nm (1.0);  $\Phi_{\text{rel}} = 0.05$ . —  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 3.0$  and  $3.6$  [m, 8H, 1(2,9,10)-H], 6.42, 6.70, 6.90, and 7.2–7.6 (m, 20H). —  $^{13}\text{C NMR}$  (62.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 33.4, 34.5$  [–, C-1(2,9,10)], 126.5, 127.1, 127.5, 128.7, 129.3, 129.5, 130.2, and 133.6 (+), 137.4, 137.9, 138.2, and 139.5 ( $\text{C}_{\text{quat}}$ ). — MS (70 eV):  $m/z$  (%) = 412 (54) [ $\text{M}^+$ ], 206 (92), 205 (100).

**4,12(15)-(2-Methoxycarbonylviny)[2.2]paracyclophane (10b)**: 800 mg (2.18 mmol) of **4**, 1.4 g (10 mmol) of  $\text{K}_2\text{CO}_3$ , 1.34 g (4.8 mmol) of  $\text{Bu}_4\text{NBr}$ , 30 mg (0.13 mmol) of  $\text{Pd}(\text{OAc})_2$  and 1.5 ml of methyl acrylate are allowed to react under nitrogen in 30 ml of dry DMF 8 d at  $60^\circ\text{C}$ . Work-up as described above and CC over 100 g of silica gel (dichloromethane,  $R_f = 0.3$ ) yield 282 mg (32%) of **10b**. All spectroscopic data are in agreement with the reported values<sup>[17]</sup>.

**4,7,12(15)-Tristyryl[2.2]paracyclophane (11a)**: 900 mg (2.02 mmol) of **5-Br** and 3.5 ml (30.5 mmol) of styrene are allowed to react for 3 d at  $100^\circ\text{C}$  according to GP 1. The crude product is

subjected to CC over 80 g of silica gel [dichloromethane/PE (60/70), 3:1] yielding 384 mg (37%) of **11a** [ $R_f = 0.46$ , dichloromethane/PE (60/70), 1:1]. Recrystallization from toluene affords 280 mg of **11a** (27%), m.p.  $185^\circ\text{C}$  (dec.). — UV (dichloromethane):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ) = 236 nm (4.512), 279 (4.512), 313 (4.460), 386 (4.579). — Fluorescence (dichloromethane, excitation at 386 nm):  $\lambda_{\text{max}}$  (rel. intensity) = 436 nm (1.0), 454 (0.99);  $\Phi_{\text{rel}} = 0.55$ . —  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.9$ – $3.6$  (m, 8H),  $6.5$ – $7.5$  (m, 26H). —  $^{13}\text{C NMR}$  (62.5 MHz,  $\text{CDCl}_3$ ): 33.2, 33.4, 33.8, and 34.5 [–, C-1(2,9,10)], 125.4, 125.9, 126.2, 126.6, 126.7, 126.8, 127.6, 128.0, 128.76, 128.81, 129.0, 131.0, 131.5, 131.8 (+), 136.3, 137.2, 137.3, 137.66, 137.70, 137.9, 138.27, 138.33, 139.5 ( $\text{C}_{\text{quat}}$ ). — MS (70 eV):  $m/z$  (%) = 514 (100) [ $\text{M}^+$ ], 308 (50), 307 (98). —  $\text{C}_{40}\text{H}_{34}$  (514.7): calcd. C 93.38, H 6.62; found C 92.97, H 6.86.

**4,7-Dibromo-12,15-distyryl[2.2]paracyclophane (12a)**: 1.0 g (1.9 mmol) of **2** and 3.5 ml (30.5 mmol) of styrene are allowed to react for 8 h at  $100^\circ\text{C}$  according to GP 1. CC over 80 g of silica gel [dichloromethane/PE (60/70), 4:1] yields fraction I ( $R_f = 0.25$ ): 214 mg (20%) of crude **12a**. Recrystallization from heptane gives 145 mg (14%) of pure **12a**. —  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.8$  (m, 2H), 3.1 (m, 2H), 3.35 (m, 2H), 3.65 (m, 2H),  $6.5$ – $7.5$  (m, 18H). — MS (70 eV):  $m/z$  (%) = 572/570/568 (50/65/50) [ $\text{M}^+$ ], 205 (100). — II ( $R_f = 0.1$ ): 500 mg (43%) of **6a**.

**4,7-Di-*p*-methoxycarbonylstyryl-12,15-di-*p*-methoxystyryl[2.2]-paracyclophane (13)**: 1.05 g (2.00 mmol) of **3** is treated with 690 mg (4.00 mmol) of methyl *p*-vinylbenzoate under nitrogen in 40 ml of dry DMF for 2 d at  $90^\circ\text{C}$  according to GP 1. Then 1.1 g (8.0 mmol) of *p*-methoxystyrene and 20 mg (0.09 mmol) of  $\text{Pd}(\text{OAc})_2$  are added and the mixture is heated for additional 4 d to  $90^\circ\text{C}$ . CC over 100 g of silica gel [dichloromethane/PE (60/70), 1:1,  $R_f = 0.25$ ] yields 150 mg (10%) of **13**, orange-yellow solid, m.p.  $245^\circ\text{C}$  (dec.). — IR (KBr):  $\tilde{\nu} = 2929 \text{ cm}^{-1}$ , 1718, 1604, 1511. — UV (dichloromethane):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ) = 287 (4.421), 364 (4.626), 398 (4.618) nm. — Fluorescence (dichloromethane, excitation at 399 nm):  $\lambda_{\text{max}}$  (rel. intensity) = 534 (1.0) nm. —  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.90$  (m, 4H), 3.61 (m, 4H), 3.90 (s, 6H,  $\text{OCH}_3$ ), 3.98 (s, 6H,  $\text{OCH}_3$ ), 6.70–8.15 (m, 16H). —  $^{13}\text{C NMR}$  (63 MHz,  $\text{CDCl}_3$ ):  $\delta = 29.7$  (–), 33.2 (–), 52.1 and 55.5 (+), 76.5, 77.0, and 77.5 ( $\text{C}_{\text{quat}}$ ), 114.3, 123.2, 126.4, 127.8, and 127.9 (+), 128.9 ( $\text{C}_{\text{quat}}$ ), 130.1 (+), 130.4, 136.6, 136.8, 137.4, 138.5, 142.1, 159.5, and 166.9 ( $\text{C}_{\text{quat}}$ ).

**4,7,12,15-Tetrakis(phenylethynyl)[2.2]paracyclophane (14)**: Under nitrogen a mixture of 1.0 g (1.9 mmol) of **3**, 1.9 g (19 mmol) of phenylacetylene, 33 mg (0.17 mmol) of copper(I) iodide and 100 mg (0.08 mmol) of tetrakis(triphenylphosphane)palladium(0) in 30 ml of dry triethylamine is heated in a capped pyrex tube 3 d to  $60^\circ\text{C}$ . Work-up corresponding to GP 1 and CC over 200 g of silica gel [i. PE (60/70), ii. dichloromethane/PE (60/70), 1:1] yield fraction I [ $R_f = 0.5$ , PE (60/70)]: phenylacetylene, not isolated. — II [ $R_f = 0.05$  in PE (60/70), 0.43 in dichloromethane/PE (60/70), 1:1]: 810 mg of **14** (70%), reddish brown solid, m.p.  $210^\circ\text{C}$ . — IR (KBr):  $\tilde{\nu} = 2930 \text{ cm}^{-1}$ , 1596, 1496, 1442, 755, 689. — UV (dichloromethane):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ) = 230 nm (4.696), 274 (4.494), 315 (4.646, sh), 346 (4.752). — Fluorescence (dichloromethane, excitation at 346 nm):  $\lambda_{\text{max}}$  (rel. intensity) = 415 nm (1.0). —  $^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 3.15$  and  $3.65$  [m, 8H, 1(2,9,10)-H], 7.20 (s, 4H, phane-arene-H), 7.30–7.70 (m, 20H, phenyl-H). —  $^{13}\text{C NMR}$  (62.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 32.7$  [–, C-1(2,9,10)], 89.3 and 94.6 ( $\text{C}_{\text{quat}}$ , C-alkyne), 123.7 and 125.2 ( $\text{C}_{\text{quat}}$ ), 127.9, 128.2, 128.4, 128.5, 131.6, and 134.7 (+), 141.9 ( $\text{C}_{\text{quat}}$ ). — MS (70 eV):  $m/z$  (%) = 608 (100) [ $\text{M}^+$ ]. —  $\text{C}_{48}\text{H}_{32}$ : calcd. 608.2504, found 608.2510 (MS).

**4,7,12,15-Tetraphenyl[2.2]paracyclophane (anti-[2.2](2',5')-*p*-Terphenylophane, 15)<sup>[13]</sup>**: 525 mg (1.00 mmol) of **3**, 65 mg (0.18

mmol) of dichlorobis(triphenylphosphane)nickel and 10 ml (10 mmol) of phenylmagnesium bromide (1 M in THF) are refluxed in 80 ml of THF for 12 h. The reaction mixture is decomposed with 100 g of ice, and 10 ml of dil. hydrochloric acid is added. The mixture is extracted with 3 × 50 ml of dichloromethane, the combined organic phases are dried with MgSO<sub>4</sub>, filtered and the solvent is evaporated in vacuo. The solid residue is subjected to CC over 100 g of silica gel [dichloromethane/PE (60/70), 1:1, R<sub>f</sub> = 0.1] and subsequently recrystallized from toluene yielding 31 mg (6%) of **15**. The spectroscopic data correspond to those reported<sup>[13]</sup>. — <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 7.27–7.45 (m, 20H, phenyl-H), 6.86 (s, 4H), 3.17 (AA'BB', 8H). — <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>): δ = 33.4, 126.7, 128.5, 129.1, 132.4, 137.0, 139.9, 140.7. — MS (70 eV): *m/z* (%) = 512 (20) [M<sup>+</sup>], 256 (100) [M<sup>2+</sup>].

**2,5-Dimethyl-1,4-distyrylbenzene (16)**: To a mixture of 2.00 g (7.6 mmol) of 2,5-dibromo-1,4-dimethylbenzene, 3.96 g (38 mmol) of styrene, 5.25 g (38 mmol) of K<sub>2</sub>CO<sub>3</sub>, 2.45 g (7.6 mmol) of Bu<sub>4</sub>NBr, 0.32 g (7.6 mmol) of lithium chloride, and 30 ml of anhydrous DMF in a capped pyrex bottle, saturated with nitrogen, is added after 20 min 136 mg (0.61 mmol) of Pd(OAc)<sub>2</sub>. The vigorously stirred mixture is heated to 110°C for 5 d, diluted with 400 ml of dichloromethane and washed with 6 portions of water (150 ml each). The organic phase is dried with MgSO<sub>4</sub> and filtered, solvents and excess of styrene are removed in vacuo. The residue is taken up in 50 ml of dichloromethane/PE (40/80), 1:1, the mixture filtered over 30 g of silica gel and the filtrate concentrated. CC of the raw product (2.10 g) over 200 g of silica gel (column 26 × 5 cm, pentane/dichloromethane, 14:1) yields fraction I (R<sub>f</sub> = 0.55): 1.32 g (61%) of 4-bromo-2,5-dimethylstilbene, yellow crystals. — <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.35 (s, 3H, CH<sub>3</sub>), 2.39 (s, 3H, CH<sub>3</sub>), 6.97 (d, *J* = 16 Hz, 1H, olefin-H), 7.21 (d, *J* = 16 Hz, 1H, olefin-H), 7.29–7.39 (m, 4H, phenyl-H), 7.44 (s, 1H, phenyl-H), 7.51 (d, *J* = 7.3 Hz, 2H, phenyl-H).

II (R<sub>f</sub> = 0.22): 0.69 g (29%) of **16**, yellow needles. For analytical purposes a small sample was recrystallized from ethanol, m.p. 195°C. — UV (dichloromethane): λ<sub>max</sub> (lg ε) = 234 nm (4.271), 353 (4.615). — Fluorescence (dichloromethane, excitation at 355 nm): λ<sub>max</sub> (rel. intensity) = 404 nm (1.0), 426 (0.98). — <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.44 (s, 6H, CH<sub>3</sub>), 7.02 (d, *J* = 16 Hz, 2H, olefin-H), 7.22–7.39 (m, 8H, olefin- and phenyl-H), 7.43 (s, 2H, phenyl-H), 7.53 (d, *J* = 8 Hz, 4H, phenyl-H). — <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>): δ = 19.54 (2 CH<sub>3</sub>), 126.11 (2 C), 126.53 (4 C), 127.19 and 127.52 (2 C), 128.67 (4 C), 129.48, 133.54, 135.51, and 137.75 (2 C). — MS (70 eV): *m/z* (%) = 310 (100) [M<sup>+</sup>], 217 (8.3), 202 (5.0), 155 (4.7) [M<sup>2+</sup>], 91 (4.8). — C<sub>24</sub>H<sub>22</sub> (310.4): calcd. C 92.86, H 7.15; found C 92.74, H 7.18.

**2,5-Dimethyl-1,4-bis(phenylethynyl)benzene (17)**: To a solution of 2.11 g (8.0 mmol) of 2,5-dibromo-1,4-dimethylbenzene, 2.29 g (22.4 mmol) of phenylacetylene, 84 mg (0.32 mmol) of triphenylphosphane, and 10 mg (0.05 mmol) of copper(II) acetate monohydrate in 16 ml of anhydrous diisopropylamine, kept in a nitrogen atmosphere, is added 16 mg (0.09 mmol) of Pd(OAc)<sub>2</sub>. The mixture is stirred and refluxed for 18 h, diluted with 200 ml of dichloromethane and washed with 5 portions of water (100 ml each). The

organic phase is dried with MgSO<sub>4</sub>, filtered and the solvent evaporated in vacuo. The residue is taken up in 50 ml of dichloromethane, filtered over 50 g of silica gel and the filtrate evaporated to dryness. CC over 200 g of silica gel (column 26 × 5 cm, pentane/dichloromethane, 14:1). — UV (dichloromethane): λ<sub>max</sub> (lg ε) = 233 nm (4.289), 313 (4.567, sh), 328 (4.652), 346 (4.502). — Fluorescence (dichloromethane, excitation at 320 nm): λ<sub>max</sub> (rel. intensity) = 353 nm (1.0), 371 (0.69). — <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.47 (s, 6H, CH<sub>3</sub>), 7.31–7.38 (m, 8H, phenyl-H), 7.50–7.57 (m, 4H, phenyl-H). — <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>): δ = 20.02 (2 CH<sub>3</sub>), 88.31 and 94.51 (2 C≡C), 122.94, 123.40, and 128.27 (2 C), 128.36 and 131.50 (4 C), 132.60 and 137.25 (2 C). — MS (70 eV): *m/z* (%) = 306 (100) [M<sup>+</sup>], 291 (8.6) [M<sup>+</sup> – CH<sub>3</sub>], 289 (10.9), 153 (5.9) [M<sup>2+</sup>]. — C<sub>24</sub>H<sub>18</sub> (306.4): calcd. C 94.08, H 5.92; found C 94.07, H 5.96.

\* Dedicated to Professor Eckerhard V. Dehmlow on the occasion of his 60th birthday.

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