Double-Layered 1,4-Distyrylbenzene Chromophores — Synthesis, UV and Fluorescence Spectra

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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 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[11] or intense charge-transfer absorptions. The response of a composite chromophor to light is strongly influenced by the relative orientation of its subunits. Chemical bonds between chromophoric subunits can generate composite chromophors of fixed geometry with enhanced charge-transfer interaction. This has been verified inter alios by Staab et al.[2] using the [2.2]paracyclophane skeleton to hold two chromophoric units at close distance with a rigid geometry. In view of the strong π-π-interaction between the aromatic rings in [2.2]paracyclophane[3], one can think of an electronic coupling between two chromophors "clamped" together at such a distance. As 1,4-distyrylbenzene[6] is a well established commercially available laser dye, we have set out to test the spectrosopic 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[5]. 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 π-system, this transformation corresponds 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[8].
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[8], 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[9], the dibromide 4 and tribromide 5 gives derivatives with one, two or three styryl or acrylate substituents (9a, 9b, 10a, b and 11a, b).

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

<table>
<thead>
<tr>
<th>Bromoarene</th>
<th>Alkene[a]</th>
<th>Product</th>
<th>R</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>styrene</td>
<td>6a</td>
<td>C₆H₅</td>
<td>45[b]</td>
</tr>
<tr>
<td>3</td>
<td>styrene</td>
<td>7a</td>
<td>C₆H₅</td>
<td>70</td>
</tr>
<tr>
<td>8</td>
<td>styrene</td>
<td>9a</td>
<td>C₆H₅</td>
<td>48[b]</td>
</tr>
<tr>
<td>4</td>
<td>styrene</td>
<td>10a</td>
<td>C₆H₅</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>styrene</td>
<td>11a</td>
<td>C₆H₅</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>methyl acrylate</td>
<td>7b</td>
<td>CO₂Me</td>
<td>56</td>
</tr>
<tr>
<td>8</td>
<td>methyl acrylate</td>
<td>9b</td>
<td>CO₂Me</td>
<td>46</td>
</tr>
<tr>
<td>4</td>
<td>methyl acrylate</td>
<td>10b</td>
<td>CO₂Me</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>o-methylstyrene</td>
<td>7c</td>
<td>o-Me-C₆H₅</td>
<td>41[b]</td>
</tr>
<tr>
<td>3</td>
<td>m-methylstyrene</td>
<td>7d</td>
<td>m-Me-C₆H₅</td>
<td>30[b]</td>
</tr>
<tr>
<td>3</td>
<td>p-methylstyrene</td>
<td>7e</td>
<td>p-Me-C₆H₅</td>
<td>44[b]</td>
</tr>
<tr>
<td>3</td>
<td>p-methoxystyrene</td>
<td>7f</td>
<td>p-MeO-C₆H₅</td>
<td>46[b]</td>
</tr>
<tr>
<td>3</td>
<td>methyl p-vinylbenzoate</td>
<td>7g</td>
<td>p-MeO₂C-C₆H₅</td>
<td>7[b]</td>
</tr>
<tr>
<td>3</td>
<td>styrene</td>
<td>12a</td>
<td>C₆H₅</td>
<td>4[b]</td>
</tr>
<tr>
<td>3</td>
<td>1) methyl p-vinylbenzoate</td>
<td>12g</td>
<td>—</td>
<td>—[c]</td>
</tr>
<tr>
<td>3</td>
<td>2) p-methoxy-styrene</td>
<td>13</td>
<td>—</td>
<td>10[d][f]</td>
</tr>
</tbody>
</table>

[a] Olefins were used in excess, yields based on bromoarenes. — [b] Yield after recrystallization, yields of the crude coupling products are 10—15% higher. — [c] Not isolated. — [d] 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[10]. As a similar effect is not operative for the trans-annular 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 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.
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, 3 can be transformed with phenylacetylene to yield the double-layered analog of 1,4-bis(phenylethynyl)benzene.

Nickel-catalyzed coupling of phenylmagnesium bromide with 3 leads to the known anti-[2.2](2',5')-p-terphenylophane (15)\cite{13}, 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 ($\lambda_{max} = 394$ nm) shows a bathochromic shift of 41 nm of the long wavelength absorption band\cite{41} 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: $\Phi = 0.78$\cite{41}). 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\cite{41}.

The electronic spectra should be influenced by the torsional angles within the stilbene units, yet the steric influence...
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 (λ<sub>max</sub> = 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 cm<sup>−1</sup>) and bathochromically shifted band (λ<sub>max</sub> = 534 nm) is observed. The large Stokes shift of 6340 cm<sup>−1</sup> as compared to 3880 cm<sup>−1</sup> in 7a (band half width 3100 cm<sup>−1</sup>) 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 Φ of 7b is only 0.2. The absorption spectrum of 7b shows shorter wavelength bands. Replacing the ethynyl subunits in 7a by ethynyl as in tetrakis(p-phenylethynyl)[2.2]paracyclocphane (14) hypsochromically shifts both the absorption (λ<sub>max</sub> = 346 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-di-methyl-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 (λ<sub>max</sub> = 328 nm) leading to a Stokes shift of only 2220 cm<sup>−1</sup>. Its increase to 4810 cm<sup>−1</sup> 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[15].

This work was supported by the Volkswagen-Stiftung and the Fonds der Chemischen Industrie. Generous gifts of chemicals by the BASF, Bayer, Hoechst, and Degussa AG are gratefully acknowledged. We are indebted to Dr. Michael Noltemeyer, Institut für Anorganische Chemie der Georg-August-Universität Göttingen, for the X-ray crystal structure determinations. B. K.Ø. is grateful to the Studienstiftung des Deutschen Volkes for a graduate fellowship.

Experimental

1H NMR: Bruker WM 250; δ = 0 for tetramethyilsilane as internal standard, δ = 7.26 for chloroform. — 13C NMR: Bruker WM 250; δ = 77 for deutériochloroform; 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 (λ = 0.71069 µm, θ/2θ 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 [× 10<sup>4</sup>] and equivalent isotropic thermal parameters [pm<sup>2</sup> × 10<sup>12</sup>] for non-hydrogen atoms of 4,7,12,15-tetraphyleny[2.2]paracyclophe (2) with e.s. d.'s of the least significant figure in parentheses; equivalent isotropic U<sub>eq</sub> defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor
atomic coordinates and equivalent isotropic thermal parameters [\text{pm}^2] for non-hydrogen atoms are given in Tables 2 and 3.

4.7.12.15-Tetramethyl[2.2]paracyclophane (2): C_{20}H_{20}Br, 523.9 g mol\(^{-1}\), monoclinic crystals, space group P21/n, \(Z = 2\), unit cell dimensions \(a = 769.7(1), b = 1276.9(3), c = 812.1(1) \text{pm}, \beta = 110.41(1)^\circ\), \(V = 748.0(2) \cdot 10^6 \text{pm}^3, U_{	ext{eq}} = 2.33 \text{ g cm}^{-3}\), 2348 observed reflections with \(2\Theta < 45^\circ, \text{MoK}α, R_w = 0.73\%\).

4.7.12.15-Tetramethyl[2.2]paracyclophane (7a): C_{20}H_{20}Br, 616.8 g mol\(^{-1}\), triclinic crystals, space group P1, \(Z = 2\), unit cell dimensions \(a = 912.2, b = 1139.9(1), c = 1705.0(2) \text{pm}, \alpha = 90.27(1), \beta = 99.09(1), \gamma = 96.30(1)^\circ, V = 1733.5(3) \cdot 10^6 \text{pm}^3, U_{	ext{eq}} = 1.182 \text{ mg cm}^{-3}\), 3419 observed reflections with \(2\Theta < 45^\circ, \text{MoK}α, R_w = 5.74\%\).

4.7.12.15- and 4.5.12.13-Tetramethyl[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°C. — IR (KBr): \(\nu = 2936 \text{ cm}^{-1}, 1439, 1064, 839\).

- \(\text{H NMR} \ (250 \text{ MHz, CDCl}_3): \delta = 3.10 \text{ and } 3.38 \text{ [m, } 8\text{H} , 1(2,9,10)-\text{H}], 7.00 \text{ (s, } 4\text{H, phase-arene-H)}. - ^{13}\text{C} \text{NMR} \ (62.5 \text{ MHz, CDCl}_3): \delta = 34.6 \text{ [-, } C(1,2,9,10), 128.7 \text{ (+, C-phenarene), 129.3 \text{ and } 140.7} \text{ (Cquan)} - \text{MS (70 eV): } m/z \text{ (%) = 528/526/524/522/520 (4/12/22/12/12) [M^+]}, 264/262/260 (44/100/44) [M^2+]. - C_{20}H_{20}Br (5239).

-c caled. 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 \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)] (Rf = 0.33), white solid, m.p. > 280°C. — \(\text{H NMR} \ (250 \text{ MHz, CDCl}_3): \delta = 3.00 \text{ to } 3.50 \text{ [m, } 8\text{H} , 1(2,9,10)-\text{H}], 7.28 \text{ (s, } 4\text{H, phase-arene-H)}. - ^{13}\text{C} \text{NMR} \ (62.5 \text{ MHz, CDCl}_3): \delta = 32.5 \text{ [-, } C(1,2,9,10), 134.5 \text{ (+, C-phenarene), 140.4} \text{ (Cquan)}.

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 1 \((R_f = 0.55) 432 mg (8.2\%) of 4,12-dibromo[2.2]paracyclophane (4)), \(\text{H NMR} \ (250 \text{ MHz, CDCl}_3): \delta = 2.80 \text{ to } 3.60 \text{ [m, } 8\text{H}, 1(2,9,10)-\text{H}], 6.48 \text{ (m, } 4\text{H}, 7.18 \text{ (m, } 2\text{H}). - ^{13}\text{C} \text{NMR} \ (62.5 \text{ MHz, CDCl}_3): \delta = 32.8 \text{ and } 35.4 \text{ [-, } C(1,2,9,10), 126.7 \text{ (Cquan)}, 128.3, 134.1 \text{ and } 137.3 \text{ (+, C-phenarene), 141.2} \text{ (Cquan)} - \text{MS (70 eV): } m/z \text{ (%) = 368/366/364/18(38/18) [M^+]} , 184/182 (96/100). - \text{II} \text{ (R} = 0.42) 1.9 g (30%) of 4,7,12,14-dimethyl[2.2]paracyclophane (5), m.p. > 280°C. — \(\text{H NMR} \ (250 \text{ MHz, CDCl}_3): \delta = 2.82 \text{ to } 3.31 \text{ [m, } 8\text{H}, 1(2,9,10)-\text{H}], 6.40 \text{ to } 7.38 \text{ (m, } 5\text{H}). - ^{13}\text{C} \text{NMR} \ (62.5 \text{ MHz, CDCl}_3): \delta = 32.3, 32.8, 33.1, 33.3, 34.5, 35.1, \text{ and } 36.8 \text{ (-, } 124.97, 125.01 \text{ and } 126.4 \text{ (Cquat), 127.8, 128.6, 129.1, 129.3, 130.9, 131.0, 132.0, 133.8, 136.5, 137.0, \text{ and } 138.2 \text{ (+, C-phenarene), 140.8} \text{ (Cquan)} - \text{MS (70 eV): } m/z \text{ (%) = 448/444/442/442 (6/20/20/6) [M^+], 184/182 (96/100). - \text{III} \text{ (R} = 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 (K_{2}CO_{3}), 4.0 mmol of tetra-n-butylammonium bromide (Bu_{4}NBr), the given amount of the appropriate alkene and 25 mg (0.11 mmol) of palladium acetate [Pd(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 (MgSO₄), filtered and the solvent is evaporated in vacuo. Chromatography of the crude products over silica gel and subsequent recrystallization afford the pure compounds.

4.7.12.15-Tetra(o-methylstyryl)[2.2]paracyclophane (7a): 1.05 g (2.0 mmol) of 3 is treated with 50 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 (Rt = 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): υ = 2927 cm⁻¹, 1495, 754, 691. — UV (dichloromethane): λₘₐₓ (lg ε) = 238 nm (4.578), 286 (4.466), 339 (4.690), 355 (4.671), 394 (4.747). — Fluorescence (dichloromethane, excitation at 394 nm): λₘₐₓ (rel. intensity) = 465 nm (1.0); Φₑₒₒ = 0.6. — ¹H NMR (250 MHz, CDCl₃): δ = 2.83-3.70 [m, 8H, 1(2,9,10)-H], 4.61 (d, ²J = 6.0 Hz, 4H, 1H, -H). — ¹³C NMR (62.5 MHz, CDCl₃): δ = 127.0, 127.5, 128.9, 130.5 C (m), 131.8 (s), 132.8, and 133.9 (Cquan) — MS (70 eV); m/z (%) = 538 (83) [M⁺], 274 (100). — C₄₉H₴₀ (673.0) : calcd. C 92.86, H 7.14; found C 92.87, H 6.72.

4.7.12.15-Tetra(m-methylstyryl)[2.2]paracyclophane (7b): 1.0 g (1.9 mmol) of 3 is treated with 50 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, Rt = 0.35]. Recrystallization from toluene/toluene (1:1) yields 750 mg of 7b (30%), yellow crystals, m.p. 192°C. — IR (KBr): υ = 3050 cm⁻¹, 2922, 1600, 979. — UV (dichloromethane): λₘₐₓ (lg ε) = 238 nm (4.599), 292 (4.521), 337 (4.724), 395 (4.717). — ¹H NMR (400 MHz, CDCl₃): δ = 2.28 (s, 3H, CH₃), 2.33 (s, 9H, CH₃), 2.81 and 3.52 [m, 8H, 1(2,9,10)-H], 6.80-7.30 (m, 28H). — ¹³C NMR (100 MHz, CDCl₃): δ = 21.1 (+, CH₃), 33.1 [-, C-1(2,9,10)], 123.5, 123.6, 125.1, 126.5, 127.6, 128.1, 128.4, 128.8, 130.1 (+), 136.7, 137.7, 138.3 (Cquan) — MS (70 eV); m/z (%) = 672 (96 [M⁺]), 336 (100). — C₅₂H₄₈ (763.0) : calcd. C 92.86, H 7.14; found C 92.87, H 7.27.

4.7.12.15-Tetra(p-methylstyryl) [2.2]paracyclophane (7c): 1.0 g (1.9 mmol) of 3 is treated with 50 ml (44 mmol) of p-methylstyrene 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, Rt = 0.40] and recrystallization from heptane/toluene (1:1) affords 562 mg of 7c (44%), yellow crystals, m.p. 188°C. — IR (KBr): υ = 3022 cm⁻¹, 2922, 1513, 959. — UV (dichloromethane): λₘₐₓ (lg ε) = 241 nm (4.558), 288 (4.445), 342 (4.701), 397 (4.762). — ¹H NMR (250 MHz, CDCl₃): δ = 2.41 (s, 12H, CH₃), 2.90 and 3.60 [m, 24H, olefin- and phenyl-H]. — ¹³C NMR (62.5 MHz, CDCl₃): δ = 13.1 [-, C-1(2,9,10)], 125.3, 126.6, 127.6, 128.1, and 128.7 (+), 136.7, 137.7, 137.9 (Cquan) — MS (70 eV); m/z (%) = 672 (90 [M⁺]), 335 (100). — C₅₂H₄₈ (763.0) : calcd. C 92.86, H 7.14; found C 92.78, H 7.17.

4.7.12.15-Tetra(p-methoxystyryl)[2.2]paracyclophane (7d): 1.0 g (2.0 mmol) of 3 and 4.83 g (36.0 mmol) of p-methoxystyrene 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, Rt = 0.25] and recrystallization from heptane/toluene (5:4) yields 670 mg of 7d (41%), yellow crystals, m.p. 250°C (dec.). — IR (KBr): υ = 3030 cm⁻¹, 2930, 2845, 1610, 1515, 1460, 1250, 1180, 1040, 840. — UV (dichloromethane): λₘₐₓ (lg ε) = 228 nm (4.565), 294 (4.481), 355 (4.739), 402 (4.795). — Fluorescence (dichloromethane, excitation at 402 nm): λₘₐₓ (rel. intensity) = 474 nm (1.0); Φₑₒₒ = 0.65. — ¹H NMR (250 MHz, CDCl₃): δ = 2.90 and 3.55 [m, 5H, 1(2,9,10)-H], 3.90 (s, 12H, OCH₃), 6.85-7.50 (m, 28H). — ¹³C NMR (62.5 MHz, CDCl₃): δ = 33.1 [-, C-1(2,9,10)], 55.4 (+, OCH₃), 114.2, 123.5, 127.8, and 128.0 (+), 130.6, 136.6, 137.5, and 139.3 (Cquan) — MS (70 eV); m/z (%) = 736 (0.3 [M⁺]), 368 (10 [M²⁺]), 122 (100). — C₅₂H₄₈O₃ (737.0) : calcd. C 84.75, H 6.57; found C 84.62, H 6.60.
subjected to CC over 80 g of silica gel [dichloromethane/PE (60/70), 3:1] yielding 384 mg (37%) of 11a [R<sub>1</sub> = 0.46, dichloromethane/PE (60/70), 1:1]. Recrystallization from toluene affords 280 mg of 11a (27%), m.p. 185°C (dec.). — UV (dichloromethane): λ<sub>max</sub> (lg e) = 236 nm (4.512), 279 (4.512), 313 (4.464), 386 (4.579). — Fluorescence (dichloromethane, excitation at 386 nm): λ<sub>max</sub> (rel. intensity) = 436 nm (1.0), 454 (0.99), Φ<sub>rel</sub> = 0.55. — 1H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.93–3.93 (m, 8H), 4.25 (t, 3H, OCH<sub>3</sub>), 7.20–7.50 (m, 20H). — MS (70 eV): m/z (%) = 514 (100) [M<sup>+</sup>].

7.4.12,15-Tetraphenyl[2.2]paracyclophane (12a): 1.0 g (1.9 mmol) of 2 and 3.5 (30.5 mmol) of styrene are allowed to react for 8 h at 100°C according to GP 1. CC over 80 g of silica gel [dichloromethane/PE (60/70), 4:1] yields fraction I (R<sub>1</sub> = 0.25) 214 mg (20%) of crude 12a. Recrystallization from heptane gives 145 mg (14%) of pure 12a. — 1H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.8 (m, 2H, 31), 2.4 (m, 2H, 1, 2H, 1, 2H), 3.6–5.7 (m, 18H). — MS (70 eV): m/z (%) = 572/570/568 (50/65/50) [M<sup>+</sup>]. 205 (100). — II (R<sub>1</sub> = 0.1): 500 mg (43%) of 6a.

These results indicate that the reaction yields the desired products with high purity and yield. The spectroscopic data are in agreement with the reported values.
mmol) of dichlorobis(triphenylphosphine)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 MgSO₄, filtered, and the solvent evaporated in vacuo. The solid residue is subjected to CC over 100 g of silica gel [dichloromethane/PE (60/70), 1:1; Rf = 0.1] and subsequently recrystallized from toluene yielding 31 mg (6%) of 2,5-Dimethyl-1,4-distyrylbenzene (16).

NMR (250 MHz, CDCl₃): δ = 2.47 (s, 6H, CH₃), 7.31 – 7.38 (m, 8H, olefin- and phenyl-H), 7.43 (s, 2H, phenyl-H), 7.50 – 7.57 (m, 4H, phenyl-H). ¹³C NMR (62.9 MHz, CDCl₃): δ = 33.4, 124.7, 127.8, 128.5, 132.9, 137.0, 135.9, 140.7. – MS (70 eV): m/z (%) = 512 (20) [M⁺], 256 (100) [M₂⁺].

I (Rf = 20.02; 0.69 g (29%) of 16, yellow needles. For analytical purposes a small sample was recrystallized from ethanol, m.p. 195°C. – UV (dichloromethane): λmax (lg e) = 234 nm (4.271), 353 (4.615). – Fluorescence (dichloromethane, excitation at 355 nm): λmax (rel. intensity) = 306 (100) [M⁺], 289 (10.9), 153 (5.9) [M₂⁺]. – C₂₉H₃₄ (306.4): calcd. C 94.08, H 5.92; found C 94.07, H 5.96.

Dedicated to Professor Eckehard V. Dehmow on the occasion of his 60th birthday.

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-57099, the names of the authors, and the journal citation.

In contrast to ref.¹⁰ we have used the cheaper tetraethylammonium bromide instead of the chloride with good results.

The authors, and the journal citation.


¹⁶ J. Teffery, Tetrahedron Lett. 1985, 26, 2667–2670. – [¹⁷] In contrast to ref.¹⁰ we have used the cheaper tetrabutylammonium bromide instead of the chloride with good results.
