# One-Pot Preparation of [*n*]Ladderanes by [2π + 2π] Photocycloaddition[‡]

**Henning Hopf,*[a] Helmut Greiving,[b] Christian Beck,[c] Ina Dix,[a] Peter G. Jones,[d] Jean-Pierre Desvergne,[e] and Henri Bouas-Laurent[e]**

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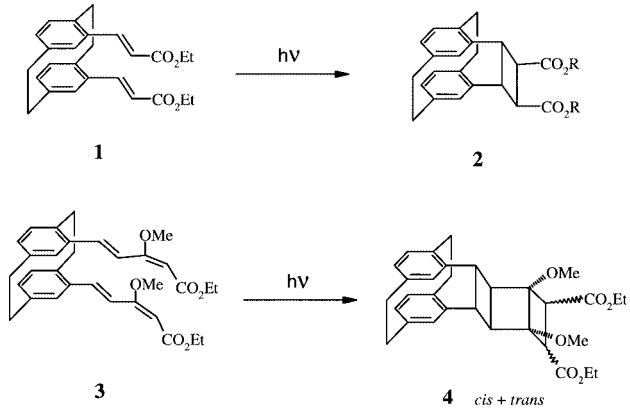
A new method for the preparation of [*n*]ladderanes is presented, based on a one-pot [2π+2π] photocycloaddition of [2.2]paracyclophane pseudo-*gem* bis(polyene) precursors. [3]- and [5]ladderanes could be isolated and were fully characterized, including their X-ray structure analysis. The overall chemical yields from [2.2]paracyclophane as starting material were found to be 53 % ([3]ladderane) and 38 % ([5]ladderane). Preliminary investigations of their photochromic properties (reversible change from yellow or red to colourless forms) are described.



## 1. Introduction

In preceding publications[1,2] dealing with the photochemistry of cinnamophane **1** and its dimethoxyvinylogue **3**, it was shown that both compounds **1** and **3** undergo intramolecular [2π+2π] photocyclization in high chemical yield (Scheme 1). The first reaction was found to be stereospecific[2] but the second led to a mixture of stereoisomers (**4**), probably because of the presence of the methoxy substituents.[1]

Compound **4** is the first [3]ladderane[3] to be obtained by photochemistry. It occurred to us that the non-methoxy substituted diene **7**, despite a possibly more difficult synthetic access, might display a stereospecific photocyclization. We were also interested to explore this new method to prepare [*n*]ladderanes for $n > 3$. Indeed, [*n*]ladderanes[3] (vide infra) are molecular systems interesting as *linear rigid spacers* and *energy-rich compounds* due to the presence of several strained small rings;[4] other known linear rods include the staffanes,[5] *p*-[*n*]cubane-1,4-diyls,[6] and spirocyclobutane-based linear backbones.[7]




Scheme 1. Intramolecular [2+2] photoadditions of cinnamophanes

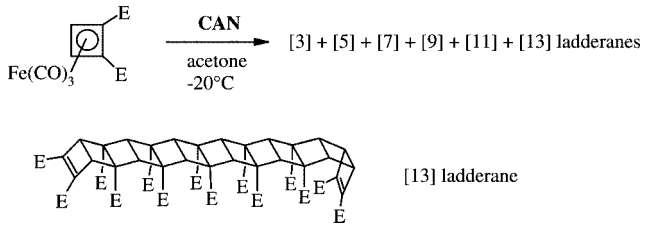
Interesting preparations of [*n*]ladderanes were published by Mehta and coworkers[3b,3c,8] based on the polymerization of a cyclobutadiene diester, generated from its iron tricarbonyl complex; it forms a mixture of oligomers that can be separated by column chromatography (Scheme 2).

Another strategy was devised by Warrener and coworkers[9] using a multistep process outlined in Scheme 3.

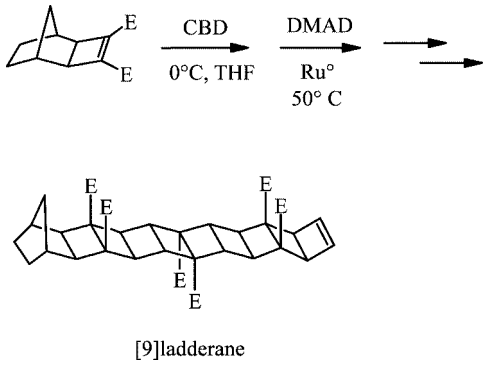
[*n*]Ladderanes were recently used as scaffolds for a photophysical study of the intermolecular interactions between pending naphthalene rings, conferring on them restricted freedom of mutual orientation.[10] Amazingly, ladderanes have been discovered in some membranes of certain bacteria;[11] the most abundant lipid is the methyl ester of a [5] ladderane $C_{20}$ fatty acid (Figure 1). Their presence makes the membrane exceptionally dense and resistant to diffusion.

[‡] Photoactive Cyclophanes, IV. Part III: Ref.[1]

[a] Institut für Organische Chemie, Technische Universität Braunschweig,
Postfach 3329, 38023 Braunschweig, Germany
Fax: (internat.) +49-531-391-5388
E-mail: h.hopf@tu-bs.de
[b] Institut für Organische Chemie, Technische Universität Braunschweig,
Postfach 3329, 38023 Braunschweig, Germany
Fax: (internat.) +49-531-391-5388
E-mail: helmut.greiving@bayerhealthcare.com
[c] Strategic and Commercial Intelligence, KPMG Deutsche Treuhand-Gesellschaft,
Marie-Curie-Straße 30, 60439 Frankfurt am Main, Germany.
E-mail: cbeck@kpmg.com
[d] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig,
Postfach 3329, 38023 Braunschweig, Germany
Fax: (internat.) +49-531-391-5387
E-mail: p.jones@tu-bs.de
[e] Laboratoire de Chimie Organique et Organométallique, UMR 5802, Université Bordeaux 1,
351 Cours de la Libération, 33405 Talence, Cedex France
Fax: (internat.) +33-5-40006646
E-mail: jp.desvergne@lcoo.u-bordeaux1.fr




Scheme 2. Synthetic Scheme for the preparation of [*n*]ladderanes from an iron tricarbonyl complex of cyclobutadiene as a suspension in acetone; the high concentration allows the formation of a nanosized product ($l$ = 1.6 nm), E = $CO_2Me$, CAN = ceric ammonium nitrate




Scheme 3. Stepwise synthesis of [*n*]ladderanes starting from a norbornane fused cyclobutene-3,4-dicarboxylic ester to which cyclobutadiene (CBD) is added initially; the major product is then reacted with excess dimethyl acetylenedicarboxylate (DMAD) in the presence of a $Ru^0$ catalyst. Repeated application of the tandem sequence allowed the preparation of various ladderanes up to [9]ladderane; E = $CO_2Me$

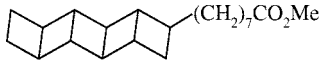



Figure 1. [5]Ladderane $C_{20}$ fatty ester found in a bacterial membrane

Ladderane structures have also been found in *inorganic crystals* such as a zigzag ladder CuI polymer,[12] a simple ladder tin phosphate built up of a four-membered cyclic tecton ($Sn_2P_2O_4$),[13] and an $Al_4N_4$ ladder tin phosphate shaped core characterized in a crystal of tetranuclear aluminium hydrazide derivative.[14]

Our preliminary results on [3]- and [5]ladderanes related to compound **4**, obtained by intramolecular photocyclization, were presented in a short communication.[15]

In this article, we describe the full details of the synthesis and spectroscopic and photochemical properties of the pseudo-*gem* dienes, trienes and tetraenes as anticipated precursors of [*n*]ladderanes, and also their potential photochromic properties.

## 2. Synthesis of Cinnamophane Vinylogs

### 2.1. Route Using Cinnamophane 1 as the Starting Material

As developed in preceding publications,[1,2] cinnamophane **1** was prepared from 4,5-diformyl[2.2]paracyclophane, obtained by chromatographic separation from a mixture of the four regioisomeric bis-formyl paracyclophanes (resulting from the Hopf synthesis of [2.2]*para*-cyclophanes).[16] To avoid the lengthy separation it was desirable to prepare the diene system **7** directly (see Scheme 5 below) using the appropriate Wittig–Horner reaction shown in Scheme 4.

But the attempt met with failure giving only poor yields of the desired products, presumably for steric reasons. It was hence advisable to move the aldehyde functions away from the cyclophane nucleus. As outlined in Scheme 5, the two ester functions of compound **1** were first reduced with DIBAL-H to diol **5** and the latter was then oxidized with $MnO_2$ to dialdehyde **6**. Subsequently the diene system could be smoothly obtained, the diethyl ester **7** in 80 % and the dimethyl ester **8** in 93 % yield. Although the spectroscopic data of **7** (see especially the $^1H$ NMR spectrum below) leave little doubt as to its *all-trans* configuration, the dimethyl ester was prepared in order to obtain single crystals suitable for X-ray structure analysis (see Section 5). The *overall yields* in **7** and **8** in three steps (54 and 61 %, respectively) are satisfactory but probably could be optimised.

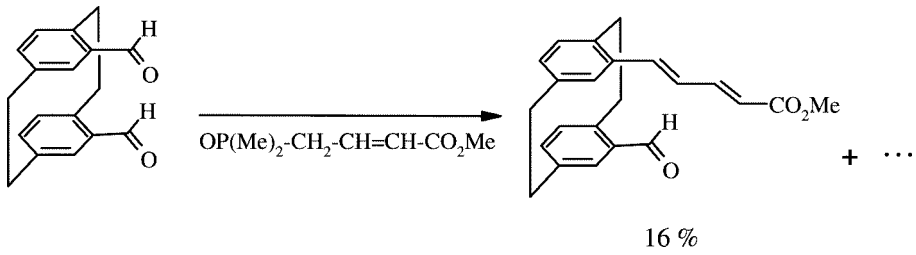
It is known that the Wittig–Horner reaction is highly stereoselective and provides very little *cis*-configured side-products. Compound **7**, obtained in analytically pure form by recrystallization, was characterized by NMR spectroscopy using 2D, H COSY and C,H-correlation (in $CDCl_3$). Some salient features (Figure 2) point to the *all-trans* configuration, the coupling constant being $>$ 15 Hz. Noteworthy also is the high coupling constant of protons 18 and 19, revealing coplanarity between the double bonds in solution.

The same strategy, applied to the other vinylogues (Scheme 5) allowed the synthesis of trienes **11** and **12** and of tetraene **15**; the latter is a deep orange, high melting (188 °C) solid. Single crystals suitable for X-ray analysis could be obtained (see Section 5); therefore, the *dimethyl* ester preparation was not attempted. Spectroscopic data, detailed in the experimental part, are in agreement with the structures proposed.

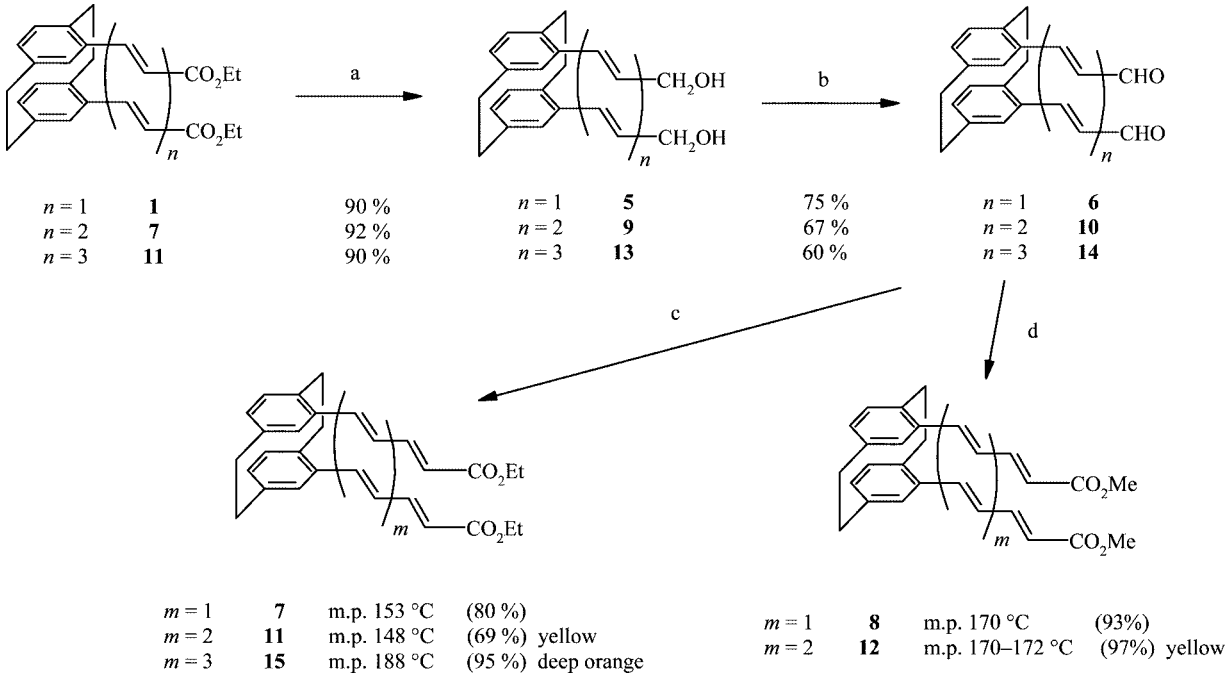
### 2.2. Direct Preparation of Pseudo-*gem* Derivatives from [2.2]Paracyclophane

An alternate route to pseudo-*gem* derivatives, involving the dialdehydes **6**, **10** and **14**, as precursors of the diester target molecules, is presented in Scheme 6. The starting material here is the parent system [2.2]paracyclophane (**16**), a commercial product.

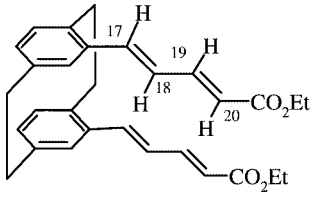
A one-pot reaction leads first to the methyl carboxylate **17** (Scheme 6);[17] its electron-withdrawing properties deactivate the positions of its own ring vis-à-vis an electrophilic substitution at the unfunctionalized ring and strongly orientates formylation towards the pseudo-*gem* position, as described in a previous publication;[17c] the ester aldehyde **18** thus obtained was easily reduced to the 4,15-diol **19**, which was smoothly oxidized to the 4,15-diformyl derivative **20**




Scheme 4. Wittig–Horner reaction on 4,15-diformyl[2.2]paracyclophane




Scheme 5. Synthetic pathway for the preparation of bi-, tri-, and tetraene systems **7**, **8**, **11**, **12** and **15** (overall yields from **1**: 54, 63, 42, 60 and 51 %, respectively). a) DIBAL-H, $Et_2O$, –80 °C; b) $MnO_2$, $CH_2Cl_2$; c) $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF; d) $(MeO)_2P(O)CH_2CO_2Me$, THF




$\delta_{H17}$ : 6.89
$\delta_{H18}$ : 6.52 $J_{17,18}$ = 15.4 Hz
$\delta_{H19}$ : 7.34 $J_{18,19}$ = 11.2 Hz
$\delta_{H20}$ : 5.89 $J_{19,20}$ = 15.2 Hz

Figure 2. Some salient features of the $^1H$ NMR spectrum showing the *all-trans*-configuration of diene **7**

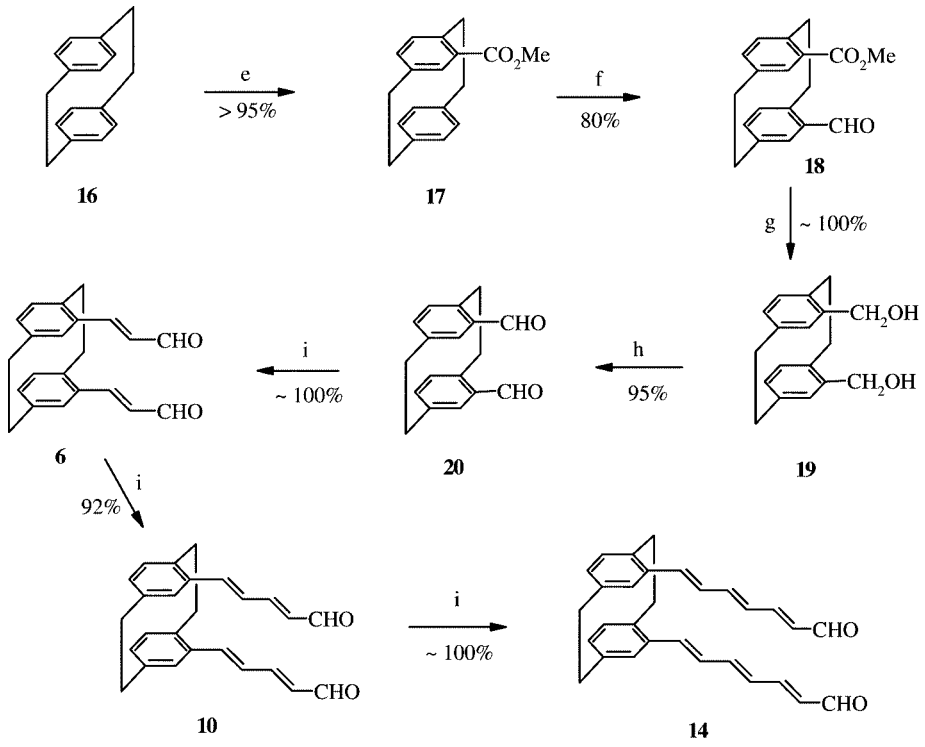
using the Dess–Martin[18] periodinane reactant (better yields than with the less expensive manganese dioxide reactant).

The vinylogous dialdehydes **6**, **10**, and **14** were prepared using (1,3-dioxolan-2-ylmethyl) triphenylphosphonium bromide, a commercial product, in the presence of potassium tert-butoxide in THF; in a second stage, the aldehyde groups were set free in acidic medium.

## 3. Electronic Absorption Spectroscopy

This section gives a short and qualitative aspect of the UV/Vis spectroscopy of the prepared [2.2]paracyclophane derivatives. The spectra of the pseudo-*gem* diesters **1**, **7**, **11**, and **15** in acetonitrile are represented in Figure 3. In line with preceding studies,[2] the long wavelength absorption bands presumably result from a Davydov splitting between the polarized transitions of the two polyenic ester substituents which form an angle close to 0°;[2] the two new transitions are then blue- and red-shifted, respectively, whereby the shorter wavelength bands ($\lambda_{max.}$ at 289, 311, 344 and 366 nm respectively, are more intense ($\varepsilon$ = 3.1 × $10^4$ to 1.1 × $10^5$ $M^{-1}$ $cm^{-1}$) than the longer wavelength absorption ($\varepsilon$ ca. 6.3 × $10^3$ to ca. 2.1 × $10^4$ $M^{-1}$ $cm^{-1}$). As the number of the conjugated double bonds increases, one observes bathochromic shifts and a hyperchromic effect, as expected.[19] But to get a deeper insight into the band assign-




Scheme 6. Direct synthesis of pseudo-*gem* derivatives **6**, **10**, and **14** from [2.2]paracyclophane (**16**); overall yields: **6** (72 %); **10** (66 %); **14** (66 %); e)[17b] (1) $(COCl)_2$, $AlCl_3$, $CH_2Cl_2$; (2) refluxing $C_6H_5Cl$; (3) MeOH, $CH_2Cl_2$; f)[17c] $Cl_2CHOCH_3$, $TiCl_4$, $CH_2Cl_2$; g) $LiAlH_4$, THF, 0 °C; h) 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (Dess–Martin periodinane), $CH_2Cl_2$; i) (1) 1,3-dioxolan-2-ylmethyltriphenylphosphonium bromide, KO*t*Bu, THF; (2) HCl, THF/$H_2O$

ment, a more extensive study including the influence of temperature would be necessary.

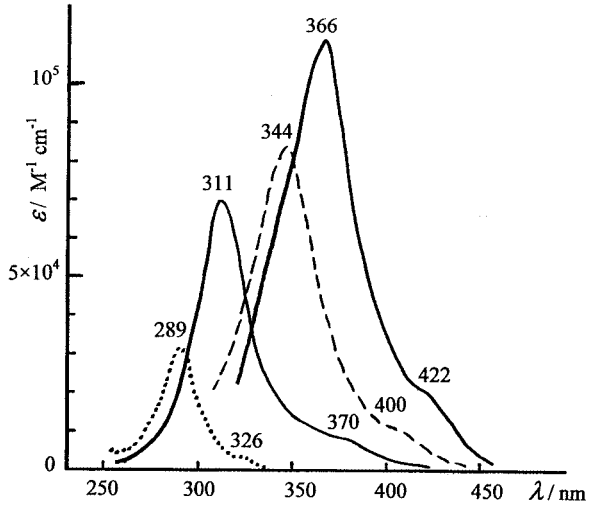



Figure 3. UV/Vis absorption spectra of pseudo-*gem* diesters **1**, **7**, **11** and **15** in acetonitrile (conc. ca. $10^{-4}$ M) between 250 and 500 nm, at ambient temperature

The fluorescence intensity from **7** to **15** was found to be very low (at the detection limit of our equipment), as expected for a polyene where the multiplication of rotation modes increases the number of radiationless channels.

## 4. Photochemistry of Cinnamophane Vinylogs 7, 11, and 15

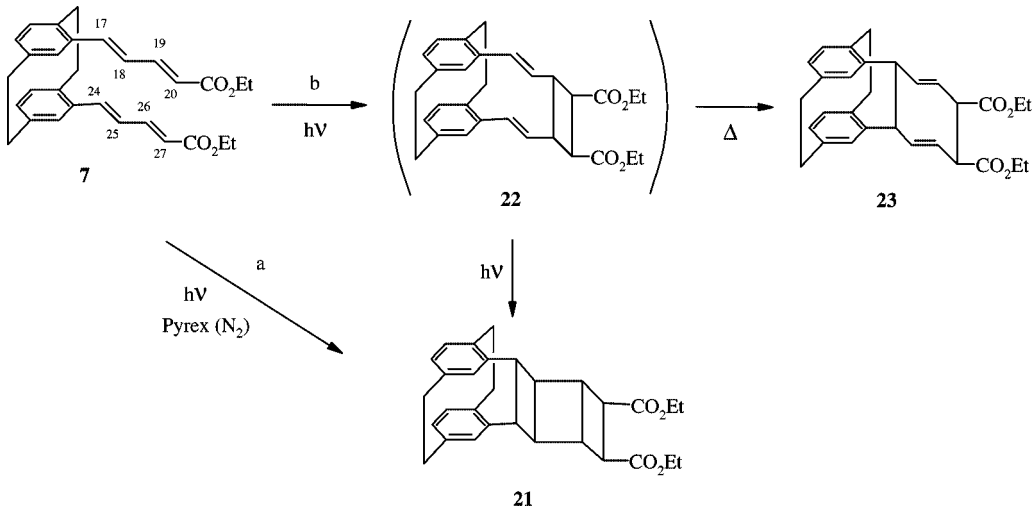
### 4.1. Diene Ester 7

A pale yellow solution of **7** in ethanol ($10^{-3}$ M) was first irradiated *with a high-pressure mercury lamp* in a Pyrex flask as optical filter at ambient temperature while nitrogen was bubbled through the reaction solution. A single photoproduct **21** was isolated in 92 % yield (Scheme 7). Its [3]ladderane structure **21** was determined by spectroscopy, elemental analysis and X-ray structural analysis (vide infra).

A second irradiation experiment of **7** in methanol ($10^{-3}$ M) was also conducted at ambient temperature but *in the daylight*, until the solution became colourless. In addition to **21**, another product was isolated and characterized as **23** (Scheme 7) displaying a cyclooctadiene structure which is tentatively assigned as the *trans, trans* strained isomer because the four vinylic protons give a multiplet ("broad singlet") at $\delta$ = 6.07 ppm (18-H, 19-H, 25-H and 26-H) and the weak (not measurable) $^3J_{HH}$ coupling constants point to the presence of angles close to 90°.

Compound **23** must result from a Cope rearrangement from a postulated intermediate **22** which, on further irradiation, should lead to **21**. This hypothesis is in keeping with previous results from Green, Lahav and Schmidt[20] on the photochemistry of butadiene derivatives in the solid state.




Scheme 7. a) 150-W high pressure mercury lamp. [**7**] ≈ $10^{-3}$ M in ethanol; b) daylight irradiation, [**7**] ≈ $10^{-3}$ M in methanol

In order to isolate such a hypothetical intermediate, another irradiation in daylight was effected using a chemical filter [aqueous solution of $Pb(OAc)_2$ and NaBr[21] cutting off all UV-light], in the expectation that **22** would not absorb light. Thin layer chromatography of the raw product revealed the presence of negligible amounts of **21** and **23**.

The $^1$H NMR spectrum of the raw product showed also signals characteristic of *trans*-double bonds ($\delta$ = 5.95 ppm, $^3J$ = 15.8 Hz) and cyclobutane rings (multiplet at $\delta$ = 4.34–4.35 ppm; these data agree with the presence of **22** but the photoproduct could not be separated).

The difference between route (a), leading to **21** as the sole product and route (b), providing a mixture of **21** and **23**, may be explained as follows: the daylight photon flux is not sufficient to generate two consecutive cyclobutane rings fast enough, so that intermediate **22** undergoes a thermal Cope rearrangement in competition with the second photocylization between position 17–18 and 24–25. It is believed that the first [2π + 2π] cycloaddition occurs between the 19–20 and 26–27 positions because the resulting intermediate **22** can still absorb light significantly in Pyrex. In contrast, the high pressure mercury lamp emits a large photon flux, and the second photocyclization occurs faster that the Cope rearrangement.

The photoreaction was followed by UV/Vis absorption spectroscopy at $\lambda$ = 345 nm, at $10^{-5}$M in methanol as a function of time (see Figure 4).

One observes three isosbestic points and the formation of a new band with $\lambda_{max.}$ at ca. 270 nm whereas the 313 nm absorption of **7** decreases steadily. The spectrum of **21** (see Figure 6) presents a maximum at ca. 230 nm. The first photoproduct spectrum shown in Figure 4 must be that of **22**. The disappearance quantum yield, (6; $\varphi_R$) measured at 320 nm, was found to be 0.20 in acetonitrile and 0.25 in methylcyclohexane. No simple explanation can be found for this slight difference (assuming it is significant). In any case, despite its stereospecificity, the photocyclization of **7** is much less efficient than that of **1** ($\varphi$ = 0.8).[2]

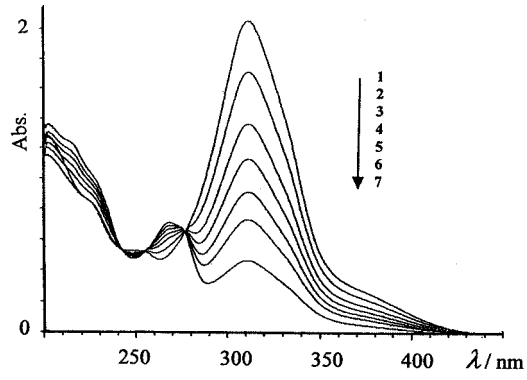



Figure 4. Electronic absorption spectra recorded as a function of time (every 10 s) during the irradiation of **7** ($10^{-5}$ M in methanol) at $\lambda$ = 345 nm

Irradiation of **21** in a quartz cell at 270 nm was found to lead to a *photostationary state* with a few % increase of the 313 nm band. This result precludes the consideration of **7** as a good *photochromic* compound. Triene **11** and tetraene **15** were observed to have a better photochromic behaviour (vide infra).

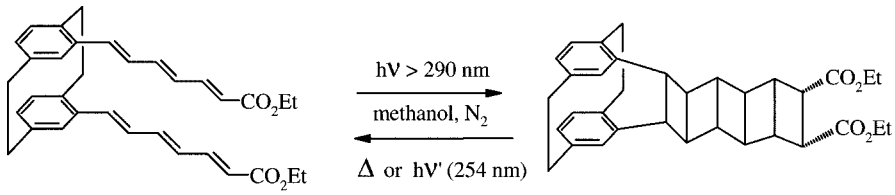
### 4.2. Triene Ester 11

Compound **11** was irradiated, under the same conditions as diene **7** (see Scheme 8) with a high pressure mercury lamp, to obtain [5]ladderane **24**, which was isolated in 83 % yield after discarding a small amount of oligomers.

The structure of **24** rests on spectroscopic data (see experimental part) and on X-ray structure determination (vide infra). As in the preceding case, the photoreaction was followed by recording the UV/Vis absorption spectra of a $10^{-5}$ M methanol solution irradiated at $\lambda$ = 345 nm as a function of time (Figure 5).

The intensity decrease of the 344 nm band is accompanied by the appearance and growth of an absorption




**11** deep yellow

**24** [5] ladderane colourless

Scheme 8. Preparation of [5]ladderane (**24**) by irradiation of a $5 \times 10^{-4}$ M methanol solution of **11** in Pyrex with a 450-W high pressure mercury lamp. **24** can revert back to **11** by heating or irradiation at shorter wavelengths

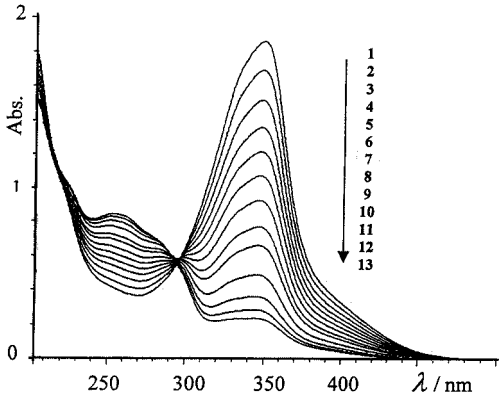



Figure 5. Electronic absorption spectra of **11** recorded as a function of time: every 10 s (1–9) and 20 s (10–13), in methanol, conc. ca. $10^{-5}$ M, at 345 nm

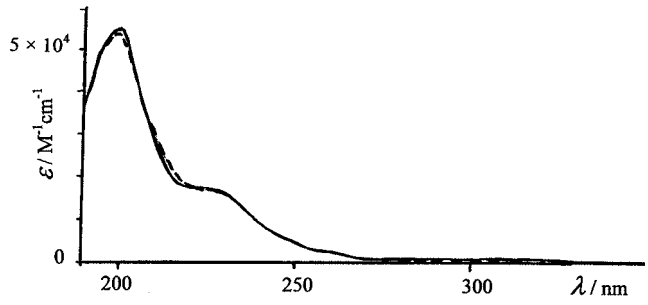


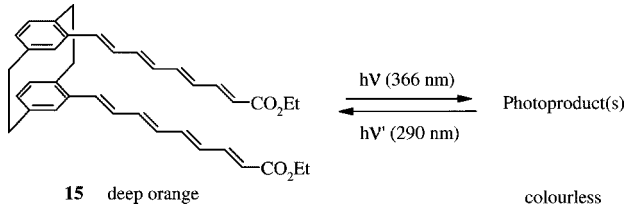

Figure 6. Electronic absorption spectra of [3]ladderane (**21**) and [5] ladderane (**24**) in acetonitrile

at 240–290 nm. The reaction appears to be clean but the spectra shown do not by themselves allow characterization of the species formed. The absorption of the product is not that of [5]ladderane. The absorption spectra of the latter and of [3]ladderane in acetonitrile are represented in Figure 6. They are very similar to each other (within the limit of experimental errors) and do not differ from that of compound **2**.[2] Although they display a tail down to 350 nm, their absorption becomes significant in the region 190–270 nm. The disappearance quantum yield ($\varphi_R$) at 345 nm was found to be 0.06 in acetonitrile and 0.08 in methylcyclohexane, a sharp decrease compared with that of diene ester **7** and in keeping with the increase of internal conversion channels with the number of double bonds.

To gain a first impression of the photochromic properties, the reverse reaction **24** → **11** was investigated qualitatively. Thermally colourless **24** was observed under the microscope to turn yellow at ca 180 °C and the yellow product was identified as **11**. Therefore, by definition,[22] **11** is a "*negative (or inverse)" photochromic compound*. By irradiation at 270 nm of a methanolic solution of **11**, pre-irradiated at 345 nm, one notes growth of the band culminating at 344 nm until a photostationary state is reached. Similar observations were made using thin layer chromatography: by irradiating a spot of **24** at 254 nm and eluting the product with $CH_2Cl_2$, it was shown that **11** was produced as a single product.

### 4.3. Tetraene Ester 15

The anticipated [7]ladderane was expected to show UV absorption comparable to that observed for [3]- (**21**) and [5]- (**24**) ladderane, respectively (see Figure 6). Therefore irradiation with visible light should not lead to a photostationary state. Irradiation of a methanolic solution in a Pyrex vessel (in the presence or absence of a chemical filter of the UV light) with a high pressure mercury lamp led to the complete disappearance of the deep-orange colour, but also the appearance of a new band culminating at $\lambda$ = 300 nm. After extraction and separation of some oligomer by-products, the resulting yellowish crude product showed the presence of broad olefinic signals and no characteristic cyclobutane peaks. No definite pure product could be isolated. Other attempts failed to improve upon this result. Nevertheless, the disappearance quantum yield of a degassed acetonitrile solution of **15** was determined at 366 nm and found to be *ca* 0.01. The photochromic properties of




**15** deep orange colourless

Scheme 9. Bleaching of **15** by irradiation at ≥ 350 nm and back reaction from the colourless product (unknown structure) at 290 nm

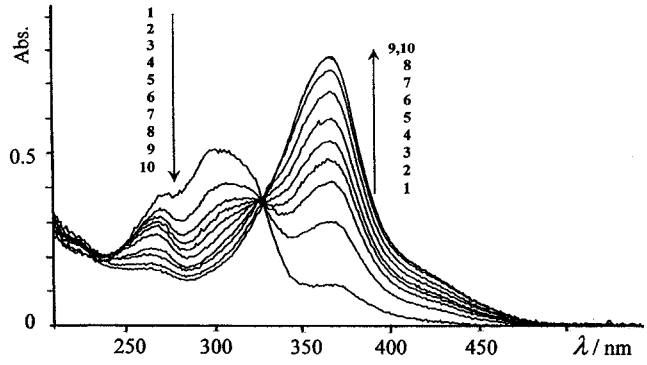



Figure 7. Curve 1 was recorded after 75 min irradiation of a $10^{-5}$ M acetonitrile solution of **15** at 366 nm. Curves 2–10 were scanned during irradiation of bleached **15** at 290 nm, after: 30 s, 1, 1:30, 2:30, 5, 10, 20, 40, 80 min

this system (Scheme 9) taken as a black box, were studies at two wavelengths, using a 1000 W Xenon lamp and a monochromator, at ambient temperature. A $10^{-5}$ M (non degassed) acetonitrile solution in a quartz cell was first bleached at 366 nm (for 75 min) and then irradiated at 290 nm for 80 min (Figure 7). The system was found to be reversible but after only 3 cycles, the absorbance had decreased by 50 %.

This new photochromic system is clean but lacks sensitivity (long exposure time, see Figure 7) and undergoes too much fatigue[22] for considering applications under these experimental conditions.

## 5. X-ray Crystal Structures

X-ray molecular structures of diene **8**, triene **12** (di*methyl* esters) and tetraene **15** (di*ethyl* ester) and also the [3]ladderane (**21**) and [5]ladderane (**24**) are described in this section.

### 5.1. 4,15-Bis[(1*E*,3*E*)-4-(methoxycarbonyl)buta-1,3-dienyl)[2.2]paracyclophane (8)

Single crystals of an intense yellow colour were obtained by slow evaporation of a $CH_2Cl_2$ solution of **8**; the asymmetric unit contains two molecules of **8** and two molecules of dichloromethane (Figure 8). Both independent molecules, which are closely similar, display an *all-trans*-configuration.

### 5.2. 4,15-Bis[(1*E*,3*E*,5*E*]-6-(methoxycarbonyl)hexa-1,3,5-trienyl)[2.2]paracyclophane (12)

In a similar way, single crystals of **12** having an intense orange colour were obtained by slow evaporation of a dichloromethane solution; the asymmetric unit contains one molecule of **12** and one molecule of dichloromethane. The molecular structure, reproduced in Figure 9, shows again an *all-trans*-configuration.

### 5.3. 4,15-Bis[(1*E*,3*E*,5*E*,7*E*)-8-(ethoxycarbonyl)octa-1,3,5,7-tetraenyl)[2.2]paracyclophane (15)

Compound **15** was dissolved in a mixture of $CH_2Cl_2$ and cyclohexane (1:1, v/v). Using a slow stream of nitrogen, most of the dichloromethane was evaporated at room temperature over 2 weeks. Further spontaneous evaporation for weeks gave intensely red needles, 1 to 2 cm long. The crystal structure (Figure 10) shows the expected *all-trans* configuration, except for the *cis* torsion angle of 5.0° for C34–C35–C36-O4.

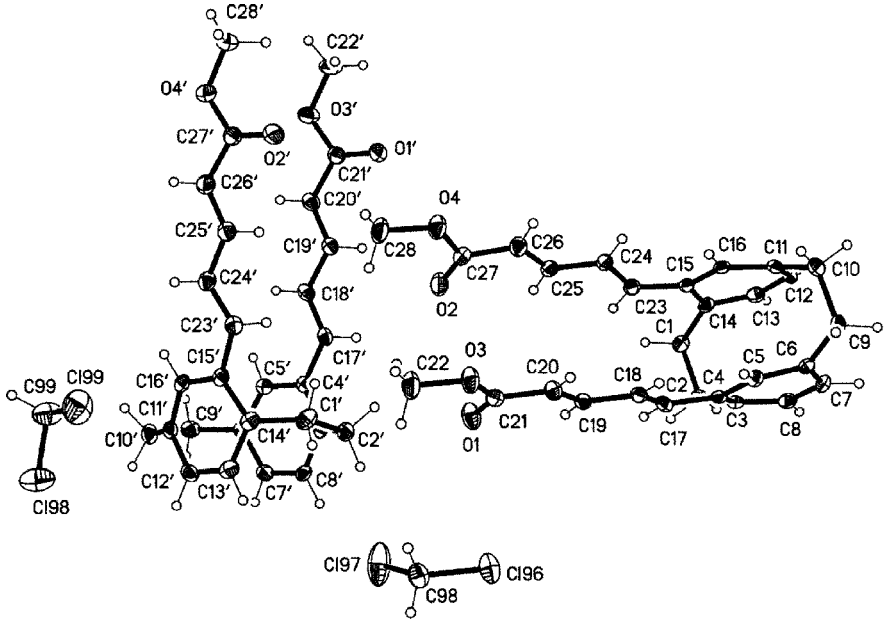



Figure 8. Structure of compound **8** in the crystal. Ellipsoids represent 30 % probability levels

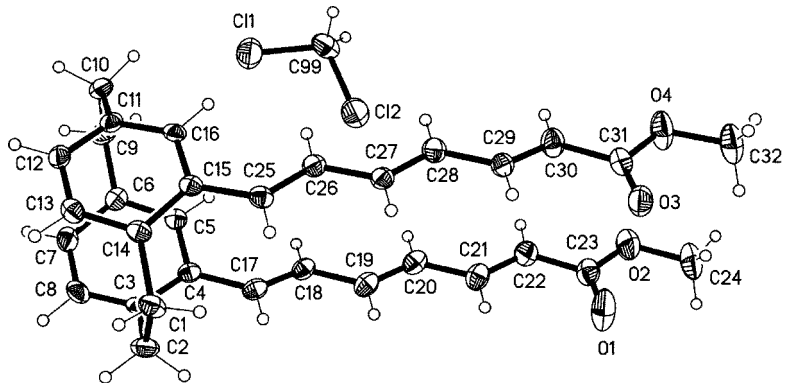



Figure 9. Structure of compound **12** in the crystal. Ellipsoids represent 30 % probability levels

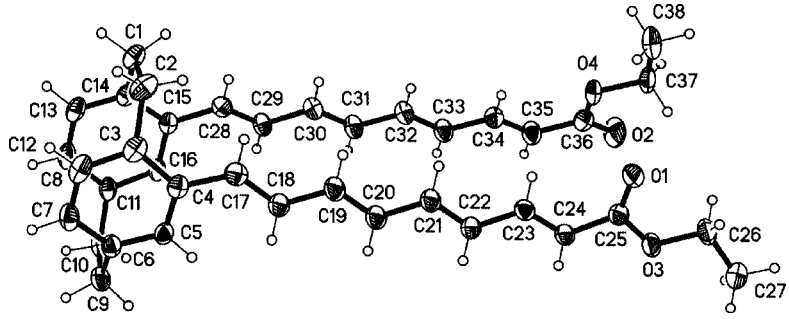



Figure 10. Structure of compound **15** in the crystal. Ellipsoids represent 30 % probability levels.

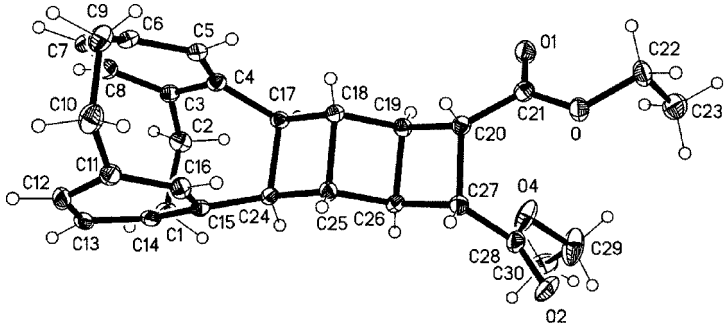



Figure 11. Structure of compound **21** in the crystal. Ellipsoids represent 30 % probability levels

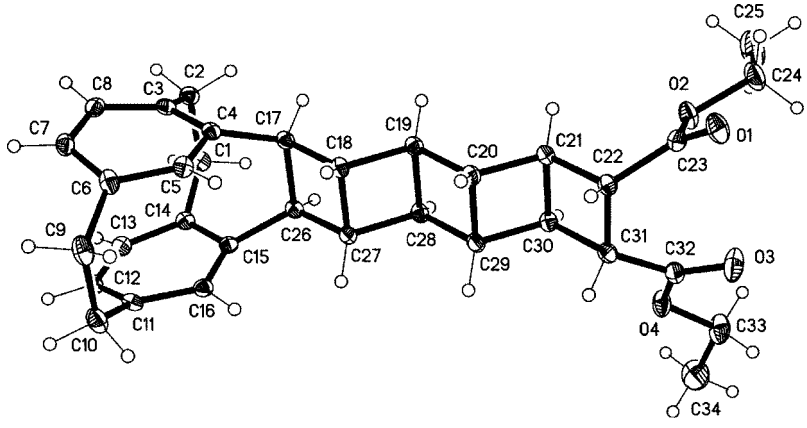



Figure 12. Structure of compound **24** in the crystal. Ellipsoids represent 30 % probability levels

### 5.4 [3]Ladderane 21

Colourless single crystals of **21** were grown from a solution in dichloromethane and ether using the vapour diffusion method. The molecular structure, represented in Figure 11, shows that the interplanar angles between the cyclobutane rings are both 113°. In the cyclobutane rings, the C–C bonds between the chains (the ladder "rungs"), especially those nearer the cyclophane, are significantly longer ($C_{17}$–$C_{24}$: 1.610(4); $C_{20}$–$C_{27}$: 156.6(5) Å] than those of the chain: 1.53–1.55 Å. One would expect that the longer bonds would be first split by heating, leading to the recovery of the starting material (see Section 4.2).

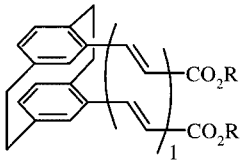
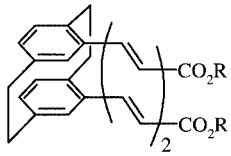
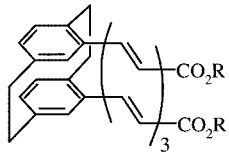
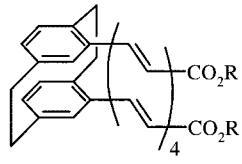
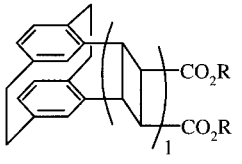
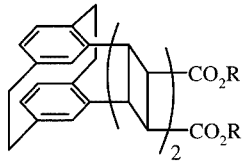
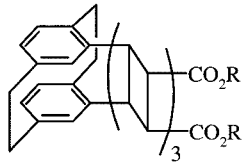
### 5.5 [5]Ladderane 24

Colourless single crystals were obtained as for the [3]ladderane **21**. The molecular structure of **24** is represented in Figure 12. It shows geometric features similar to those of [3]ladderane; of note is again the enhanced length of the interchain bond of the cyclobutane ring neighbouring the phane nucleus, C17–C26: 1.626(3) Å.

## 6. Summary and Conclusion

[3]Ladderane **21** and [5]ladderane **24** were prepared by a one-pot, light-induced reaction. The starting materials **7**

Table 1. Cinnamophane vinylogs and ladderanes; overview of the main experimental data

| | | | | |
|---|---|---|---|---|
| Starting material |  |  |  |  |
| | R = Et (**1**) | R = Me (**8**) | R = Me (**12**) | R = Et (**15**) |
| X-ray | + | + | + | + |
| m.p. R = Et | 113 °C<br>colourless | 153 °C<br>pale yellow | 148 °C<br>orange | 188 °C<br>deep orange |
| m.p. R = Me | – | 170 – 172 °C | 170 – 172 °C | – |
| $\lambda_{max}$ (log $\varepsilon$)<br>solvent<br>(R = Et) | 289 nm (4.51)<br>MeOH | 311 nm (4.85)<br>MeCN | 344 nm (4.93)<br>MeCN | 366 nm(5.1)<br>MeCN |
| photo product<br>R = Et |  |  |  | – |
| | **2** | **21**<br>[3]ladderane | **24**<br>[5]ladderane | |
| m.p. | 168 °C | 199 °C | 215 °C | |
| Quantum yield[a]<br>R = Et | 0.82 ($CH_3CN$)<br>0.80 (MeOH) | 0.25 (MCH)[b]<br>0.20 ($CH_3CN$) | 0.08 (MCH)[b] | 0.01 ($CH_3CN$) |
| chemical yield | 100% | 92% | 83% | – |
| X-ray<br>R = Et | + | + | + | – |

[a] In degassed solution. [b] Methylcyclohexane.

and **11** were synthesized in a few steps in overall yields higher than 50 % from [2.2]paracyclophane (**16**), a commercial product. It is likely that the [2π+2π] photo-cyclization is a stepwise singlet state reaction, as strongly suggested by the stereospecificity of the main product; the *chemical yields* for **2**, **21** and **24** were found to decrease slightly with the extension of the chain length: 100 %, 92 % and 83 %, respectively, whereas the disappearance quantum yields from **1**, **7**, **11** and **15** show a steep drop: 0.8, 0.2, 0.08 and 0.01, respectively (see Table 1). These quantum yields reflect the formation of intermediates rather than that of the ladderanes but point to a decrease of reactivity, in line with the multiple possible deactivation channels, such as *cis-trans* isomerization and internal conversion. Intermolecular additions (oligomerization) were found to be more and more abundant (from **7** to **11** and **15**) in keeping with the decreased intramolecular reactivity.

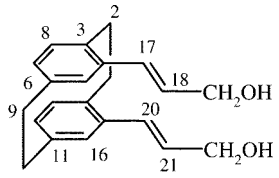
The failure to isolate the [7]ladderane sets a limit to the method of "*topochemistry in solution*" using [2.2]paracyclophane as molecular scaffold playing the role of crystal packing to direct the product stereochemistry. Mutatis mutandis, as in helicene syntheses, where Martin found a new method for preparing [7]- to [14]helicenes[23] extending the size of helicenes beyond $n = 6$ (Newman[23c]), the photochemical formation of [*n*]ladderanes with $n \geq 7$ should involve new synthetic strategies.

## 7. Experimental Section

**General:** Melting points: Büchi 510 melting point apparatus, uncorrected. Thin layer chromatography (TLC): Macherey–Nagel Polygram Sil G/UV 254 and Polygram Alox N/UV 254. Column chromatography: Merck Kieselgel 60 (70–230 mesh). IR: Perkin–Elmer 1420 or Nicolet 320 FT-IR spectrometer. $^1$H and $^{13}$C NMR: Bruker AM 400 MHz ($^1$H) and 100.6 MHz ($^{13}$C) or Bruker AC 200 ($^1$H) and 50.3 MHz ($^{13}$C); AC 250 and 62.9 MHz ($^{13}$C) in $CDCl_3$, internal standards: TMS, $\delta = 0$ ppm for $^1$H, $CHCl_3$, $\delta = 77.05$ ppm for $^{13}$C spectroscopy. UV/Vis: Beckman UV 5230 or HitachiU 3300; the samples were weighed with a Mettler UM3 balance (sensitivity $10^{-7}$ g). Fluorescence spectra, corrected for absorption and emission were taken with a Hitachi F 4500 spectrofluorimeter. Reaction quantum yields were determined as described elsewhere;[2] the samples were degassed by the freeze, pump, and thaw technique. Irradiations were conducted with high pressure mercury lamps (150 W or 450 W). Appropriate filters were used for selecting regions of the UV emissions.

**Synthesis:** (1,3-Dioxolan-2-ylmethyl)triphenylphosphonium bromide was prepared according to ref.[24] 4-Methoxycarbonyl[2.2]paracyclophane (**17**) was prepared according to ref.[25] with a longer period of heating in refluxing chlorobenzene (ca. 16 h) than indicated by the original authors (3 h) for the decarbonylation step.

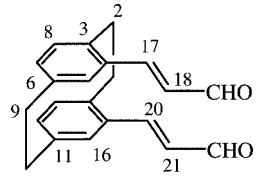
1. **4,15-Bis[(*E*)-2-hydroxymethylvinyl)[2.2]paracyclophane (5):** To a solution of **1** (1.0 g, 2.5 mmol) in diethyl ether (200 mL) at –78 °C, a hexane solution (10 mL, 10 mmol) of 1 M DIBAL-H was added dropwise under nitrogen. The mixture was warmed up to 0 °C within 1 h, was then diluted with 100 mL of ethyl acetate, and hydrolysed with 1 mL of 15 % aqueous NaOH solution and 4 mL of water. After stirring at room temp. for 2 h, the solution was filtered and the filtrate concentrated in vacuo to give a colorless solid which was recrystallized from methanol: 750 mg (2.3 mmol, 92 %) **5**, colourless plates, m.p. 168 °C.




**5**

IR (FT-IR, KBr): $\tilde{\nu} = 3330$ cm$^{-1}$ (s), 3035 (w), 2926 (s), 2854 (m), 1480 (w), 1412 (w), 1096 (m), 1010 (m), 965 (s). $^1$H NMR (200 MHz, $CDCl_3$): $\delta = 6.74$ (d, $J_{17,18} = J_{20,21} = 15.8$ Hz, 2 H, 17-H, 20-H), 6.63 (d, $J_{5,7} = J_{12,16} = 1.6$ Hz, 2 H, 5-H, 16-H), 6.50 (d, $J_{7,8} = J_{12,13} = 7.8$ Hz, 2 H, 8-H, 13-H), 6.44 (dd, $J_{7,8} = J_{12,13} = 7.8$, $J_{7,5} = J_{12,16} = 1.6$ Hz, 2 H, 7-H, 12-H), 6.00 (dt, $J_{18,17} = J_{21,20} = 15.8$, $J_{18,19} = J_{21,22} = 5.4$ Hz, 2 H, 18-H, 21-H), 4.29 (dd, $J_{19,18} = J_{22,21} = 5.4$, $J = 1.5$ Hz, 4 H, 19-H, 22-H), 3.63 3.52 (m, 2 H, 1a-H, 2a-H), 3.04 (br. s, 4 H, 9-H, 10-H), 3.07–2.94 (m, 2 H, lb-H, 2b-H) ppm. $^{13}$C NMR (50.3 MHz, $CDCl_3$): $\delta = 139.4$, 137.4, 137.0 (s, C-3, C-4, C-6, C-11, C-14, C-15), 134.6, 132.3, 130.2, 129.4, 127.9 (d, C-5, C-7, C-8, C-12, C-13, C-16, C-17, C-18, C-20, C-21), 63.6 (t, C-19, C-22), 35.1, 32.6 (t, C-1, C-2, C-9, C-10) ppm. MS (70 eV): *m*/*z* (%) = 320 (18) [M$^+$], 161 (10), 159 (22), 143 (50), 129 (100), 115 (14). UV ($CH_3CN$): $\lambda_{max.}$ (log $\varepsilon$) 217 nm (4.44), 257 (4.32), 288 (3.84, sh), 340 (2.99, sh).

2. **4,15-Bis[(*E*)-2-formylvinyl][2.2]paracyclophane (6):** A suspension of **5** (1.0 g, 3.1 mmol, freshly prepared) in dichloromethane (250 mL) and activated $MnO_2$ (10.0 g, 110 mmol)) was stirred at room temp. for 10 min under nitrogen. The mixture was filtered through a 10 cm long $Na_2SO_4$ column, and the filtrate was concentrated in vacuo to provide **6** as a yellowish rhombic solid (750 mg, 2.4 mmol, 77 %), m.p. 191 °C.



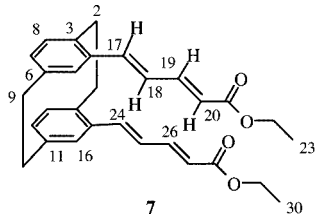

**6**

IR (KBr): $\tilde{\nu} = 3042$ cm$^{-1}$ (w), 2925 (m), 2824 (w), 2746 (w), 1691 (vs), 1677 (vs), 1617 (m), 1590 (m), 1200 (w), 1132 (s), 969 (m). $^1$H NMR (400 MHz, $CDC1_3$): $\delta = 9.59$ (d, $J_{19,18} = J_{22,21} = 7.5$ Hz, 2 H, 19-H, 22-H), 7.49 (d, $J_{17,18} = J_{20,21} = 15.8$ Hz, 2 H, 17-H, 20-H), 6.76 (br. s, 2 H, 5-H, 16-H), 6.65 (br. s, 4 H, 7-H, 8-H, 12-H, 13-H), 6.43 (dd, $J_{18,17} = J_{21,20} = 15.8$, $J_{18,19} = J_{21,22} = 7.5$ Hz, 2 H, 18-H, 21-H), 3.65–3.60 (m, 2 H, la-H, 2a-H), 3.20–3.16 (m, 2 H, lb-H, 2b-H), 3.16–3.08 (m, 4 H, 9-H, 10-H) ppm. $^{13}$C NMR (100.6 MHz, $CDC1_3$): $\delta = 193.0$ (s, C-19, C-22), 149.7, 135.7, 135.5, 131.1, 129.1 (d, C-5, C-7, C-8, C-12, C-13, C-16, C-17, C-18, C-20, C-21), 140.3, 140.0, 134.5 (s, C-3, C-4, C-6, C-11, C-14, C-15), 34.8, 32.8, (t, C-1, C-2, C-9, C-10) ppm. MS (70 eV): *m*/*z* (%) = 316 (26) [M$^+$], 159 (22), 158 (20), 157 (19), 129 (100), 128 (45), 115 (22). UV ($CH_3CN$): $\lambda_{max.}$ (log $\varepsilon$) = 222 nm (4.35), 241 (4.12), 295 (4.55), 336 (3.82, sh), 370 (3.42, sh).

3. **4,15-Bis[(1*E*,3*E*)-4-(ethoxycarbonyl)buta-1,3-dienyl][2.2]paracyclophane (7):** A suspension of NaH (0.9 g, 22.5 mmol, 60 % dispersion in mineral oil) in THF (150 mL) was cooled to 0 °C and diethyl ethoxycarbonylmethylphosphonate (5.5 g, 24.5 mmol) was added dropwise under nitrogen. After stirring at room temp. for

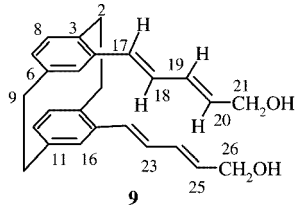
30 min, **6** (0.8 g, 2.5 mmol) was added to the reaction mixture. After stirring for another 30 min and usual workup, the crude product was chromatographed on silica gel with dichloromethane to give 0.9 g (2.0 mmol, 80 %) of **7**, yellow needles, m.p. 153 °C.



**7**

IR (KBr): $\tilde{\nu}$ = 2855 $cm^{-1}$ (w), 2868 (w), 2929 (m), 2980 (m), 3033 (w), 1705 (vs), 1620 (vs), 1243 (s), 1135 (s), 998 (m), 880 (w), 713 (w). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.34 (dd, $J_{19,18} = J_{26,25}$ = 11.2, $J_{19,20} = J_{26,27}$ = 15.2 Hz, 2 H, 19-H, 26-H), 6.89 (d, $J_{17,18} = J_{24,25}$ = 15.4 Hz, 2 H, 17-H, 24-H), 6.70 (br. s, 2 H, 5-H, 16-H), 6.52 (dd, $J_{18,19} = J_{25,26}$ = 11.2, $J_{18,17} = J_{25,24}$ = 15.4 Hz, 2 H, 18-H, 25-H), 6.50 (br. s, 4 H, 7-H, 8-H, 12-H, 13-H), 5.83 (d, $J_{20,19} = J_{27,26}$ = 15.2 Hz, 2 H, 20-H, 27-H), 4.19 (q, $J_{22,23} = J_{29,30}$ = 7.1 Hz, 4 H, 22-H, 29-H), 3.48–3.43 (m, 2 H, 1a-H, 2a-H), 3.06–2.99 (m, 6 H, 1b-H, 2b-H, 9 H, 10-H), 1.30 (t, $J_{23,22} = J_{30,29}$ = 7.1 Hz, 6 H, 23-H, 30-H) ppm. $^{13}C$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 166.8 (s, C-21, C-28), 144.7 (d, C-18, C-26), 139.7, 138.6, 136.1 (s, C-3, C4, C-6, C-11, C-14, C-15), 138.3 (d, C-17, C-24), 135.0, 133.5, 126.9 (d, C-18, C-25, C-7, C-8, C-12, C-13), 129.5 (d, C-5, C-16), 120.8 (d, C-20, C-27), 60.1 (t, C-22, C-29), 34.9 (t, C-9, C-10), 32.6 (t, C-1, C-2), 14.3 (q, C-23, C-30) ppm. MS (70 eV): *m*/*z* (%) = 456 (40) [$M^+$], 411 (16), 382 (22), 336 (20), 309 (16), 227 (94), 199 (42), 181 (100), 172 (14), 155 (60), 154 (30), 141 (24), 128 (22). UV (MeOH): $\lambda_{max.}$ (1og $\varepsilon$) = 224 nm (4.43), 254 (4.30), 312 (4.93), 380 (3.97, sh). UV ($CH_3CN$): $\lambda_{max.}$ (lg $\varepsilon$) = 224 nm (4.36), 250 (4.23), 311 (4.85), 370 (3.96, sh). UV (methylcyclohexane): $\lambda_{max.}$ (log $\varepsilon$) = 225 nm (4.35), 250 (4.23), 307 (4.79), 370 (3.79, sh). $C_{30}H_{32}O_4$ (456.62): calcd. C 78.91, H 7.08; found: C 78.82, H 7.00.

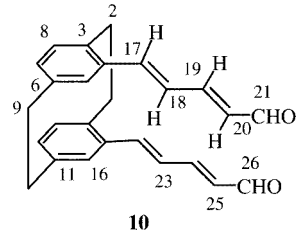
4. **4,15-Bis[(1*E*,3*E*)-4-(hydroxmethyl)buta-1,3-dienyl][2.2]paracyclophane (9):** Diester **7** (0.44 g, 0.88 mmol) was dissolved in $Et_2O$ (200 mL) and the solution cooled to 0 °C under nitrogen; after addition of 7 mL (7 mmol) of a 1M DIBAL-H/*n*-hexane solution, the mixture was warmed to 0 °C during 1 h whilst stirring. The mixture was treated with 100 mL of ethyl acetate, 4 mL of water, and 1 mL of a 15 % aqueous NaOH solution. After stirring at room temp. for 2 h, the mixture was filtered and the filtrate was concentrated in vacuo. The colorless solid residue was recrystallized from methanol to provide 0.3 g (0.81 mmol, 92 %) of **9**, colorless needles, m.p. > 250 °C (dec.).



**9**

IR (KBr): $\tilde{\nu}$ = 3427 $cm^{-1}$ (vs), 3029 (w), 2928 (m), 2856 (m), 1656 (s), 1592 (m), 1412 (w), 1277 (w), 1160 (m), 984 (m). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 6.68 (d, $J_{5,7} = J_{16,12}$ = 1.7 Hz, 2 H, 5-H, 16-H), 6.61 (d, $J_{17,18} = J_{22,23}$ = 15.1 Hz, 2 H, 17-H, 22-H), 6.48 (dd, $J_{18,17} = J_{23,22}$ = 15.1, $J_{18,19} = J_{23,24}$ = 10.2 Hz, 2 H, 18-H, 23-H), 6.48 (d, $J_{8,7} = J_{13,12}$ = 7.8 Hz, 2 H, 8-H, 13-H), 6.44 (dd, $J_{7,8} = J_{12,13}$ = 7.8, $J_{7,5} = J_{12,16}$ = 1.7 Hz, 2 H, 7-H, 12-H), 6.39 (ddt, $J_{19,20} = J_{24,25}$ = 14.8, $J_{19,18} = J_{24,23}$ = 10.2, $J_{19,21} = J_{24,26}$ = 1.4 Hz, 2 H, 19-H, 24-H), 5.84 (ddd, $J_{20,19} = J_{25,24}$ = 14.8, $J_{20,21a} = J_{25,26a}$ = 6.8, $J_{20,21b} = J_{25,26b}$ = 4.8 Hz, 2 H, 20-H, 25-H), 4.28–4.17 (m, 4 H, 21-H, 26-H), 3.50–3.45 (m, 2 H, 1a-H, 2a-H), 3.05 (br. s, 4 H, 9-H, 10-H), 3.01–2.96 (m, 2 H, 1b-H, 2b-H), 2.71 (t, $J_{OH,21} = J_{OH,26}$ = 5.6 Hz, 2 H, OH) ppm. $^{13}C$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 139.4, 137.7, 137.0 (s, C-3, C-4, C-6, C-11, C-14, C-15), 134.7, 132.3, 132.2, 131.5, 131.2, 129.3, 128.3 (d, C-5, C-7, C-8, C-12, C-13, C-16, C-17, C-18, C-19, C-20, C-22, C-23, C-24, C-25), 63.3 (t, C-21, C-26), 35.0, 32.6 (t, C-1, C-2, C-9, C-10) ppm. UV ($CH_3CN$): $\lambda_{max.}$ (log $\varepsilon$) = 221 nm (4.45), 240 (4.33), 284 (4.74), 290 (4.74), 320 (3.93, sh), 360 (3.46, sh).

5. **4,15-Bis[(1*E*,3*E*)-4-formylbuta-1,3-dienyl][2.2]paracyclophane (10):** A suspension of 0.3 g (0.81 mmol) of **9**, dissolved in 200 mL of $CH_2Cl_2$, and 10 g (110 mmol) of activated $MnO_2$ was stirred for 10 min under nitrogen. The mixture was filtered through a 10-cm $Na_2SO_4$ column in the dark, and the filtrate was concentrated in vacuo to provide after recrystallization from $CHCl_3$ 0.2 g (0.54 mmol, 67 %) of **10**, yellow solid, m.p. 230 °C.

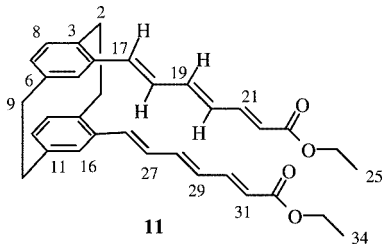


**10**

IR (KBr): $\tilde{\nu}$ = 3037 $cm^{-1}$ (w), 2928 (m), 2895 (w), 2854 (w), 2810 (w), 1674 (vs), 1611 (s), 1158 (m), 1145 (m), 1118 (m), 980 (m). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 9.53 (d, $J_{21,20} = J_{26,25}$ = 7.8 Hz, 2 H, 21-H, 26-H), 7.16 (dd, $J_{19,20} = J_{24,25}$ = 15.2, $J_{19,18} = J_{24,23}$ = 11.2 Hz, 2 H, 19-H, 24-H), 7.03 (d, $J_{17,18} = J_{22,23}$ = 15.4 Hz, 2 H, 17-H, 22-H), 6.75 (br. s, 2 H, 5-H, 16-H), 6.68 (dd, $J_{18,17} = J_{23,22}$ = 15.4, $J_{18,19} = J_{23,24}$ = 11.2 Hz, 2 H, 18-H, 23-H), 6.56 (br. s, 4 H, 7-H, 8-H, 12-H, 13-H), 6.15 (dd, $J_{20,19} = J_{25,24}$ = 15.2, $J_{20,21} = J_{25,26}$ = 7.8 Hz, 2 H, 21-H, 26-H), 3.55–3.50 (m, 2 H, 1a-H, 2a-H), 3.13–3.07 (m, 6 H, 1b-H, 2b-H, 9-H, 10-H) ppm. $^{13}C$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 193.0 (s, C-21, C-26), 151.8, 140.4, 135.2, 134.2, 131.2, 130.1, 126.9 (d, C-5, C-7, C-8, C-12, C-13, C-16, C-17, C-18, C-19, C-20, C-22, C-23, C-24, C-25), 140.0, 139.0, 135.8 (s, C-3, C-4, C-6, C-11, C-14, C-15), 34.9, 32.7 (t, C-1, C-2, C-9, C-10) ppm. MS (70 eV): *m*/*z* (%) = 368 (20) [$M^+$], 339 (12), 185 (52), 184 (36), 183 (100), 155 (86), 141 (58), 129 (66), 128 (34), 115 (22). UV ($CH_3CN$): $\lambda_{max.}$ (log $\varepsilon$) = 224 nm (4.26), 256 (4.10), 322 (4.73), 390 (3.72, sh).

6. **4,15-Bis[(1*E*,3*E*,5*E*)-6-(ethoxycarbonyl)hexa-1,3,5-trienyl][2.2]paracyclophane (11):** To a stirred suspension of NaH (0.17 g, 4.3 mmol, 60 % dispersion in mineral oil) in THF (150 mL), diethyl ethoxycarbonylmethylphosphonate (0.98 g, 4.3 mmol) was added dropwise at 0 °C under nitrogen. After the formation of the reactant was complete (30 min), 0.2 g (0.54 mmol) of **10** was added to the reaction mixture, and the stirring was continued for 30 min at room temp. After the usual workup (phase separation, extraction of the solid residue with $CH_2Cl_2$, washing with $H_2O$, desiccation with $MgSO_4$), the $CH_2Cl_2$ solution was chromatographed on silica gel, yielding 0.19 g (0.37 mmol, 69 %) of **11**, deep yellow needles, m.p. 148 °C.

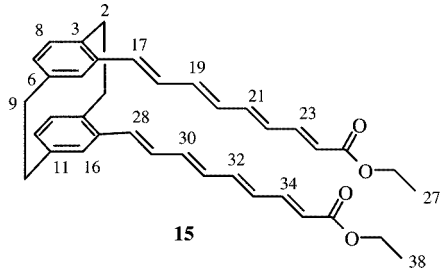
  




**11**

IR (KBr): $\tilde{\nu}$ = 3028 $cm^{-1}$ (w), 2981 (m), 2931 (m), 2856 (w), 1706 (vs), 1603 (s), 1465 (m), 1368 (s), 1301 (s), 1261 (vs), 1134 (vs), 1003 (s). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.28 (dd, $J_{21,22} = J_{30,31}$ = 15.1, $J_{21,20} = J_{30,29}$ = 11.3 Hz, 2 H, 21-H, 30-H), 6.72 (d, $J_{17,18} = J_{26,27}$ = 14.9 Hz, 2 H, 17-H, 26-H), 6.67 (br. s, 2 H, 5-H, 16-H), 6.60 (dd, $J_{19,20} = J_{28,29}$ = 14.3, 2 H, 19-H, 28-H), 6.52 (dd, $J_{18,17} = J_{27,26}$ = 15.0, $J_{18,19} = J_{27,28}$ = 10.8 Hz, 2 H, 18-H, 27-H), 6.50 (d, $J_{8,7} = J_{13,12}$ = 7.8 Hz, 2 H, 8-H, 13-H), 6.48 (dd, $J_{7,8} = J_{12,13}$ = 7.8, $J_{7,5} = J_{12,16}$ = 1.5 Hz, 2 H, 7-H, 12-H), 6.29 (dd, $J_{20,19} = J_{29,28}$ = 14.2, $J_{20,21} = J_{29,30}$ = 11.4 Hz, 2 H, 20-H, 29-H), 5.80 (d, $J_{22,21} = J_{31,30}$ = 15.2 Hz, 2 H, 22-H, 31-H), 4.19 (dd, $J_{24,25} = J_{33,34}$ = 7.1, $J$ = 1.0 Hz, 4 H, 24-H, 33-H), 3.50–3.45 (m, 2 H, la-H, 2a-H), 3.09 –3.02 (m, 4 H, 9-H, 10-H), 3.03–2.99 (m, 2 H, lb-H, 2b-H), 1.29 (t, $J_{25,24} = J_{34,33}$ = 7.1 Hz, 6 H, 25-H, 34-H) ppm. $^{13}C$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 167.0 (s, C-23, C-32), 144.3 (d, C-21, C-30), 141.2 (d, C-19, C-28), 139.6, 138.3, 136.7 (s, C-3, C-4, C-6, C-11, C-14, C-15), 134.9 (d, C-8, C-13), 134.9 (d, C-17, C-26), 133.0 (d, C-7, C-12), 130.0 (d, C-20, C-29), 129.4 (d, C-5, C-16), 128.8 (d, C-18, C-27), 120.7 (d, C-22, C-31), 60.2 (t, C-24, C-33), 35.0 (t, C-9, C10), 32.7 (t, C-1, C-2), 14.3 (q, C-25, C-34) ppm. MS (70 eV): *m*/*z* % = 508 (27) [$M^+$], 482 (6), 462 (10), 434 (14), 416 (10), 389 (12), 361 (10), 255 (24), 254 (22), 253 (100), 207 (58), 181 (66), 179 (80), 165 (60), 141 (58). UV (MeOH): $\lambda_{max.}$ (log $\varepsilon$) = 216 nm (4.37), 346 (4.97), 410 (4.09, sh). UV ($CH_3CN$): $\lambda_{max.}$ (log $\varepsilon$) = 216 nm (4.36), 344 (4.92), 400 (4.11, sh). UV (methylcyclohexane): $\lambda_{max.}$ (1log $\varepsilon$) = 217 nm (4.37), 334 (4.89), 344 (4.90). $C_{34}H_{36}O_4$ (508.70): calcd. C 80.27, H 7.15; found C 80.48, H 7.10.

7. **4,15-Bis[(1*E*,3*E*,5*E*,7*E*)-8-(ethoxycarbonyl)octa-1,3,4,5-tetraenyl]-[2.2]paracyclophane (15): a) Preparation of 13: 11** (100 mg, 0.20 mmol) was reduced with 1 M DIBAL-H/*n*-hexane solution (1.5 mL, 1.5 mmol), according to the procedure described above for **5**, to give the diol **13** (75 mg, 90 %) as yellowish needles, m.p. > 280 °C. **b) Preparation of 14:** Using the procedure described above for **6**, the diol **13** (75 mg), was oxidized with $MnO_2$ to the dialdehyde **14** (45 mg, 61 %). Orange crystals, m.p. 213 °C. **c) Preparation of 15:** The dialdehyde **14** (45 mg, 0.11 mmol) was reacted with NaH (34 mg, 0.9 mmol, 60 % in mineral oil and diethyl {(ethoxycarbonyl)methyl] phosphonate (0.20 g, 0.9 mmol) using the procedure for preparing **7**, providing 40 mg (64 %) of **15**, orange-red crystals, m.p. 188 °C.




**15**

$^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.29 (dd, $J_{23,24} = J_{34,35}$ = 15.2, $J_{23,22} = J_{34,33}$ = 11.4 Hz, 2 H, 23-H, 34-H), 6.68 (br. s, 2 H, 5-H, 16-H), 6.67 (d, $J_{17,18} = J_{28,29}$ = 14.3 Hz, 2 H, 17-H, 28-H), 6.59–6.23 (m, 14 H, 7-H, 8-H, 12-H, 13-H, 18-H, 19-H, 20-H, 21-H, 22-H, 29-H, 30-H, 31-H, 32-H, 33-H), 5.81 (d, $J_{24,23} = J_{35,34}$ = 15.2 Hz, 2 H, 24-H, 35-H), 4.20 (q, $J_{26,27} = J_{37,38}$ = 7.1 Hz, 4 H, 26-H, 37-H), 3.49–3.45 (m, 2 H, la-H, 2a-H), 3.09–2.98 (m, 6 H, lb-H, 2b-H, 9-H, 10-H), 1.30 (t, $J_{27,26} = J_{38,37}$ = 7.1 Hz, 6 H, 27-H, 38-H) ppm. $^{13}C$ NMR (100.6 MHz, $CDCl_3$): $\delta$ = 166.9 (s, C-25, C-36), 144.2 (d, C-23, C-34), 139.5, 138.0, 136.9 (s, C-3, C-4, C-6, C-11, C-14, C-15), 140.7, 137.9, 134.8, 132.6, 131.8, 129.8, 129.3 (d, C-7, C-8, C-12, C-13, C-18, C-19, C-20, C-21, C-22, C-29, C-30, C-31, C-32, C-33), 133.5 (d, C-17, C-28), 129.2 (d, C-5, C-16), 120.6 (d, C-24, C-35), 60.1 (t, C-26, C-37), 35.0 (t, C-9, C-10), 32.7 (t, C-1, C-2), 14.2 (q, C-27, C-38) ppm. MS (70 eV): *m*/*z* (%) = 560 (35) [$M^+$], 281 (20), 279 (50), 205 (58), 191 (40), 155 (32), 141 (100), 129 (50). HRMS: $C_{38}H_{40}O_4$, calcd. 560.29266; found 560.292 ± 2 ppm.

8. **4,15-Bis(hydroxymethyl)[2.2]paracyclophane (19):** To a solution of the ester aldehyde **8** (5.88 g, 0.02 mol) in 150 mL of anhydrous THF was slowly added at 0 °C 1.52 g (0.04 mol) $LiAlH_4$ in 50 mL of THF. The mixture was stirred for 15 h and warmed up to room temp. Under stirring and cooling, 50 g ice was introduced with caution and the mixture was acidified with 100 mL of 2 N $H_2SO_4$ until the aluminium hydroxide had dissolved. After the usual workup, the residue was dried in vacuo to provide 5.36 g (0.02 mol, quantitative yield) of **19** as a white microcrystalline powder, m.p. 217–219 °C, ref.[25] m.p. 208–210 °C.

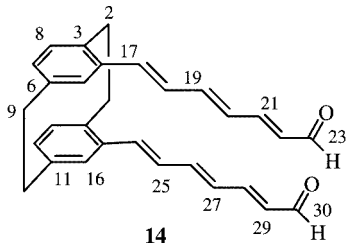
9. **4,15-Diformyl[2.2]paracyclophane (20):** To a suspension of **19** (268 mg, 1 mmol) in 20 mL of dichloromethane was added the Dess–Martin periodinane reagent (975 mg, 2.3 mmol). The mixture was stirred for ca. 30 min (TLC control), then 20 mL of saturated $Na_2S_2O_3$ solution and 20 mL of saturated $NaHCO_3$ solution were introduced. The stirring was maintained for another 30 min. After the usual workup (extraction with $CH_2Cl_2$), 250 mg (0.95 mmol, 95 %) of **20** was obtained, m.p. 207–209 °C; ref.[26] m.p.195–196 °C.

10. **4,15-Bis[(*E*)-2-formylvinyl][2.2]paracyclophane (6):** In a dry 250 mL three-necked round-bottom flask equipped with a Claisen adapter, a reflux condenser and a nitrogen inlet, 1,3-dioxolan-2-ylmethyltriphenylphosphonium bromide (15 g, 35 mmol) and KO*t*Bu (3.94 g, 35 mmol) in 50 mL of anhydrous THF were placed. The mixture was stirred for 30 min and **20** (1.1 g, 4.2 mmol) in 30 mL of THF was introduced prior to another 3 h stirring at room temp. After the mixture had been refluxed for 90 min, 160 mL of 10 % HCl was added, generating a pale flocculent precipitate. After cooling for ca. 16 h at 2 °C, the solid was removed by filtration. The filtrate was washed with water and extracted with $CH_2Cl_2$. Usual workup led to 1.32 g (4.2 mmol, quantitative yield) of **6**, m.p. 186–188 °C, comparable to the product described above, m.p. 191 °C (vide supra).

11. **4,15-Bis[(1*E*,3*E*)-4-formylbuta-1,3-dienyl][2.2]paracyclophane (10):** The procedure used for the preparation of **6** from **20** was applied; the Wittig salt (13.7 g, 32 mmol), KO*t*Bu (3.58 g, 32 mmol) and **6** (1.264 g, 4 mmol) in 110 mL of THF led to **10** (1.36 g, 3.7 mmol, 92 %) as a yellow solid, m.p. 218 °C (dec.). The spectroscopic data were identical to those described above.

12. **4,15-Bis[(1*E*,3*E*,5*E*)-6-formylhexa-1,3,5-trienyl][2.2]paracyclophane (14):** The procedure used in the preparation of **6** from **20** was applied; the Wittig salt (2.15g, 5 mmol), KO*t*Bu (560 mg, 5 mmol) and **10** (225 mg, 0.61 mmol) in 75 mL of THF led to **14** (255 mg, 0.61 mmol, quantitative yield); m.p. 227 °C (dec.), deep orange solid.

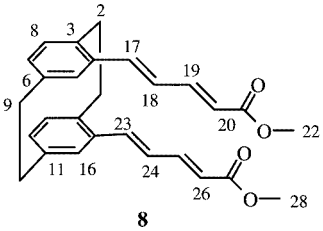
  




**14**

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.54 (d, $J_{22,23} = J_{29,30}$ = 7.8 Hz, 2 H, H-23, H-30), 7.10 (dd, $J_{20,21} = J_{27,28}$ = 11.2, $J_{22,21} = J_{29,28}$ = 15.1 Hz, 2 H, 21-H, 28-H), 6.82 (d, $J_{18,17} = J_{25,24}$ = 15.3 Hz, 2 H, 17-H, 24-H), 6.75 (dd, $J_{19,18} = J_{26,25}$ = 10.8, $J_{19,20} = J_{26,27}$ = 14.7 Hz, 2 H, 19-H, 26-H), 6.70 (br-s, 2 H, 5-H, 16-H), 6.58 (dd, $J_{19,18} = J_{26,25}$ = 10.9, $J_{17,18} = J_{24,25}$ = 15.3 Hz, 2 H, 18-H, 25-H), 6.53 (br-s, 4 H, 7-H, 8-H, 12-H, 13-H), 6.45 (dd, $J_{20,21} = J_{27,28}$ = 11.1, $J_{19,20} = J_{26,27}$ = 14.4 Hz, 2 H, 20-H, 27-H), 6.12 (dd, $J_{22,23} = J_{29,30}$ = 7.8, $J_{22,21} = J_{29,28}$ = 15.2 Hz, 2 H, 22-H, 29-H), 3.53–3.44 (m, 2 H, 1a-H, 2a-H), 3.13 –3.00 (m, 6 H, 1b-H, 2b-H, 9-H, 10-H) ppm. $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ = 193.0 (d, C-23, C-30), 151.1 (d, C-21, C-28), 143.1 (d, C-19, C-26), l39.7 (s), l38.4 (s), 136.7 (d, C-17, C-24), 136.4 (s), l35.0 (d, C-7, C-12 or C-8, C-13), 133.4 (d, C-7, C-12 or C-8, C-13), 130.9 (d, C-22, C-29), 129.8 (d, C-20, C-27), 129.7 (d, C-5, C-16), 128.4 (d, C-18, C-25), 34.9 (t, C-9, C-10), 32.7 (t, C-1, C-2) ppm. MS (70 eV): *m*/*z* (%) = 420 (31) [$M^+$], 211 (48), 209 (100), 193 (35), 181 (48), 179 (35), 165 (50), 142 (63)), 141 (78), 129 (25)), 128 (26), 115 (20), 81 (23). $C_{30}H_{28}O_2$ (420.55): calcd. C 85.68, H 6.71; found C 85.53, H 6.80.

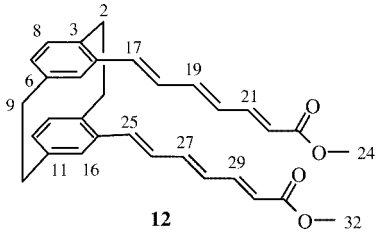
13. **4,15-Bis[(1*E*,3*E*)-4-(methoxycarbonyl)buta-1,3-dienyl][2.2]paracyclophane (8):** A suspension of NaH (90 mg, 3 mmol, 80 % in mineral oil) in 25 mL of THF was mixed with dimethyl methoxycarbonylmethylphosphonate (568 mg, 0.45 mL, 3.1 mmol) whilst stirring (strong foaming); within 5 min a viscous white suspension had formed. After 20 min, **10** (316 mg, 1 mmol) in 25 mL of THF was added and the stirring was maintained for another 20 min. 20 mL of the THF was distilled off under reduced pressure, and 50 mL of water was added, generating a precipitate that was filtered off, washed with 50 mL of water, and dried at ca. 60 °C. The crude product (0.40 g) was chromatographed on silica gel (20 g) with $CH_2Cl_2$/EtOAc, 19:1. Yield 352 mg (0.88 mmol, 88 %) of **8**, intense yellow crystals, m.p. 170–172 °C.




**8**

IR (KBr): $\tilde{\nu}$ = 3006 cm$^{-1}$ (w), 2948 (m), 2927 (m), 2890 (w), 2853 (w), 1708 (vs), 1620 (vs), 1587 (m), 1452 (w), 1434 (m), 1346 (m), l316 (m), 1297 (m), 1248 (m), 1206 (w), 1189 (m), 1177 (m), 1161 (m), 1145 (s), 1137 (vs), 1002 (m), 881 (m), 725 (w), 713 (w). $^1$H NMR (400 MHz, $CDC1_3$): $\delta$ = 7.29 (dd, $J_{18,19} = J_{24,25}$ = 11.2, $J_{20,19} = J_{26,25}$ = 15.3 Hz, 2 H, 19-H, 25-H), 6.85 (d, $J_{17,18} = J_{23,24}$ = 15.4 Hz, 2 H, 17-H, 23-H), 6.66 (s, 2 H, 5-H, 16-H), 6.48 (dd, $J_{18,19} = J_{24,25}$ = 11.2, $J_{17,18} = J_{23,24}$ = 15.4 Hz, 2 H, 18-H, 24-H), 6.46 (s, 4 H, 7-H, 8-H, 12-H, 13-H), 5.77 (d, $J_{19,20} = J_{25,26}$ = 15.3 Hz, 2 H, 20-H, 26-H), 3.68 (s, 6 H, 22-H, 28-H), 3.43–3.39 (m, 2 H, 1a-H, 2a-H), 3.02 (s, 4 H, 9-H, 10-H), 3.00–2.95 (m, 2 H, 1b-H, 2b-H) ppm. $^{13}$C NMR (100 MHz, $CDC1_3$): $\delta$ = 167.2 (s, C-21, C-27), 145.0 (d, C-19, C-25), l39.7 (s), 138.7 (s), l38.4 (d, C-17, C-23), l36.0 (s), 135.0, 133.6 (d, C-7, C-8, C-12, C-13), 129.5 (d, C-5, C-16), 126.8 (d, C-18, C-24), 120.3 (d, C-20, C-26), 51.4 (q, C-22, C-28), 34.9 (t, C-9, C-10), 32.6 (t, C-1, C-2) ppm. MS (70 eV): *m*/*z* (%) = 428 (59) [$M^+$], 396 (18), 368 (23), 336 (18), 309 (10), 213 (100), 181 (85), 155 (54), 141 (18), 128 (16), 115 (9). UV/Vis (MeCN): $\lambda_{max.}$ (log $\varepsilon$) = 226 nm (4.31), 254 (4.18), 312 (4.81), 370 (sh) (390), 394 (sh) (364). $C_{28}H_{28}O_4$: 428.52. HRMS calcd. 428.19876, found 428.198 ± 3 ppm; calcd. C 78.48, H 6.59; found C 78.42, H 6.69.

14. **4,15-Bis[(1*E*,3*E*,5*E*)-6-(methoxycarbonyl)hexa-1,3,5-trienyl][2.2]paracyclophane (12):** A suspen-sion of NaH (270 mg, 9 mmol, 80 % in mineral oil) was mixed with dimethyl ethoxycarbonylmethylphosphonate (1.71 g, 9.4 mmol, 1.35 mL) in 100 mL of THF; after stirring for ca. 25 min, a solution of **14** (1.1, 3 mmol) in 50 mL of THF was added and the stirring was maintained for another 20 min. After work-up (see above for **8**), the crude product (1.40 g) was recrystallized from a 1:1 mixture of dichloromethane and cyclohexane to give **12** (1.1 g, 2.3 mmol, 76 %) as intensely orange needles, m.p. 170–172 °C.



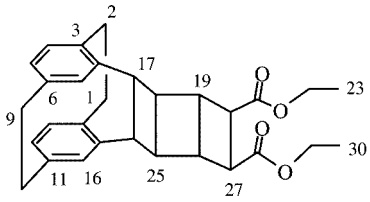

**12**

IR (KBr): $\tilde{\nu}$ = 3032 cm$^{-1}$ (w), 2939 (w), 2926 (m), 2889 (w), 2866 (w), 2849 (w), 1713 (vs), 1698 (vs), 1623 (s), 1602 (s), 1580 (m), 1433 (m), 1355 (m), 1315 (m), 1299 (m), 1262 (vs), 1220 (m), 1198 (m), 1187 (m), 1176 (m), 1137 (vs), 1045 (m), 1021 (m), 998 (vs), 968 (w), 885 (m), 850 (m), 725 (w). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.29 (dd, $J_{20,21} = J_{29,28}$ = 11.4, $J_{21,22} = J_{29,30}$ = 15.2 Hz, 2 H, 21-H, 29-H), 6.73 (d, $J_{17,18} = J_{25,26}$ = 14.8 Hz, 2 H, 17-H, 25-H), 6.68 (br-s, 2 H, 5-H, 16-H), 6.60 (dd, $J_{18,19} = J_{26,27}$ = 10.9, $J_{19,20} = J_{27,28}$ = 14.4 Hz, 2 H, 19-H, 27-H), 6.56–6.49 (dd, m, 6 H, 7-H, 8-H, 12-H, 13-H, 18-H, 26-H), 6.30 (dd, $J_{21,20} = J_{29,28}$ = 11.4, $J_{19,20,} = J_{27,28}$ = 14.3 Hz, 2 H, 20-H, 28-H), 5.80 (d, $J_{21,22} = J_{29,30}$ = 15.3 Hz, 2 H, 22-H, 30-H), 3.74 (s, 6 H, C-24, C-32), 3.50–3.45 (m, 2 H, 1a-H, 2a-H), 3.11–2.99 (m, 6 H, 1b-H, 2b-H, 9-H, 10-H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 167.3 (s, C-23, C-31), 144.5 (d, C-21, C-29), 141.3 (d, C-19, C-27), 139.6 (s), 138.3 (s), 136.6 (s), 135.0 (d, C-17, C-25), 134.9 (d, C-7, C-12 or C-8, C-13), 133.0 (d, C-7, C-12 or C-8, C-13), 129.9 (d, C-20, C-28), 129.3 (d, C-5, C-16), 128.7 (d, C-18, C-26), 120.2 (d, C-22, C-30), 51.4 (q, C-24, C-32), 35.0 (t, C-9, C-10), 32.7 (t, C-1, C-2) ppm. MS (70 eV): *m*/*z* (%) = 480 (40) [$M^+$], 448 (6), 420 (8), 239 (100), 209 (31), 207 (35), 181 (46), 179 (54), 165 (44), 141 (41). UV/Vis (MeCN): $\lambda_{max.}$ (log $\varepsilon$) = 218 mn (4.40), 366 (sh) (4.93), 346 (4.96), 382 (sh) (4.26), 430 (sh) (4.09). $C_{32}H_{32}O_4$: 480.60. HRMS calcd. 480.23006, found 480.230 ± 3 ppm; calcd. C 79.97, H 6.71; found C 79.97, H 6.85.

15. **Photochemical Preparations: a) Preparation of [3]Ladderane 21:** A sample of the diester **7** (140 mg, 0.3 mmol)) was dissolved in 250 mL of ethanol and the solution was irradiated for 30 min with a 150-W high-pressure mercury lamp fitted in a Pyrex immersion well photoreactor; the reactor was cooled by circulating water between the walls surrounding the lamp and nitrogen was bubbled through the reaction solution. After irradiation, the solvent was removed in vacuo and the residue was chromatographed on a short

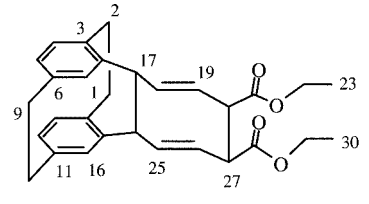
silica gel column with dichloromethane: **21** (130 mg, 0.28 mmol, 92 %), colorless needles, m.p. 199 °C.



**21**

IR (KBr): $\tilde{\nu}$ = 3002 $cm^{-1}$ (w), 2954 (s), 2931 (m), 2908 (m), 1736 (vs), 1724 (s), 1460 (m), 1365 (m), 1267 (s), 1222 (m), 1193 (s), 1153 (m), 1060 (m), 1042 (s). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 6.47 (dd, $J_{7,8} = J_{12,13}$ = 7.8, $J_{7,5} = J_{12,16}$ = 1.6 Hz, 2 H, 7-H, 12-H), 6.20 (d, $J_{8,7} = J_{13,12}$ = 7.8 Hz, 2 H, 8-H, 13-H), 6.19 (d, $J_{5,7} = J_{16,12}$ = 1.6 Hz, 2 H, 5-H, 16-H), 4.36 (br. s, 2 H, 17-H, 24-H), 4.19 (q, $J_{22,23} = J_{29,30}$ = 7.1 Hz, 4 H, 22-H, 29-H), 3.59 (br. s, 2 H, 20-H, 27-H), 3.42 (br. s, 2 H, 19-H, 26-H), 3.18 (br. s, 2 H, 18-H, 25-H), 3.15–2.96 (m, 6 H, 1a-H, 2a-H, 9-H, 10-H), 2.61–2.54 (m, 2 H, 1b-H, 2b-H), 1.30 (t, $J_{23,22} = J_{30,29}$ = 7.1 Hz, 6 H, 23-H, 30-H) ppm. $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 172.73 (s, C-21, C-28), 140.3, 140.0, 139.3 (s, C-3, C-4, C-6, C-11, C-14, C-15), 134.5, 133.0, 128.8 (d, C-5, C-7, C-8, C-12, C-13, C-16), 60.8 (t, C-22, C-29), 51.5, 46.0, 43.0, 41.9 (d, C-17, C-18, C-19, C-20, C-24, C-25, C-26, C-27), 36.2, 32.1 (t, C-1, C-2, C-9, C-10), 14.3 (q, C-23, C-30) ppm. MS (70 eV): *m/z* (%) = 456 (25) [$M^+$], 411 (30), 382 (20), 336 (20), 227 (86), 181 (100), 155 (60), 128 (22), 108 (40). UV ($CH_3CN$): $\lambda_{max.}$ (log $\varepsilon$) = 198 nm (4.74), 224 (4.24), 292 (2.95).

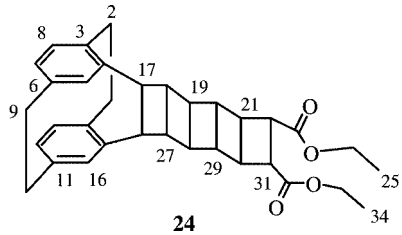
**b) Daylight Irradiation of 7:** A solution of **7** (100 mg, 0.22 mmol) in 350 mL of methanol was irradiated in an Erlenmeyer flask for 6 h in the daylight (summer in Bordeaux). After 3 h, the yellow colour had disappeared. The solution was concentrated in vacuo; the residue was dissolved in dichloromethane and chromatographed on silica gel providing two fractions: [3]ladderane (**21**), 35 mg, and a mixture of **23** + **21** (2:1), 50 mg. The spectroscopic data (NMR) of **23** could be assigned by subtraction of the data of **21**.



**23**

$^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 6.44 (dd, $J_{7,8} = J_{12,13}$ = 7.9, $J_{7,5} = J_{12,16}$ = 1.7 Hz, 2 H, 7-H, 12-H), 6.32 (d, $J_{5,7} = J_{16,12}$ = 1.7 Hz, 2 H, 5-H, 16-H), 6.28 (d, $J_{8,7} = J_{13,12}$ = 7.9 Hz, 2 H, 8-H, 13-H), 6.07 (br. s, 4 H, 18-H, 19-H, 25-H, 26-H), 4.72 (br. s, 2 H, 17-H, 24-H), 4.27 (br. s, 2 H, 20-H, 27-H), 4.25 (qd, $J_{22,23} = J_{29,30}$ = 7.1, $J$ = 1.2 Hz, 4 H, 22-H, 29-H), 3.33–3.23 (m, 2 H, 1a-H, 2a-H), 3.16 –2.97 (m, 4 H, 9-H, 10-H), 2.75–2.65 (m, 2 H, 1b-H, 2b-H), 1.33 (t, $J_{23,22} = J_{30,29}$ = 7.1 Hz, 6 H, 23-H, 30-H) ppm. $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 172.9 (s, C-21, C-28), 142.7, 140.4, 139.6 (s, C-3, C-4, C-6, C-11, C-14, C-15), 136.7, 133.2, 132.7, 129.3, 128.1 (d, C-5, C-7, C-8, C-12, C-13, C-16, C-18, C-19, C-25, C-26), 61.3 (t, C-22, C-29), 48.6, 47.1 (d, C-17, C-20, C-24, C-27), 36.4, 33.3 (t, C-1, C-2, C-9, C-10), 14.2 (q, C-23, C-30) ppm.

**c) Preparation of [5]Ladderane (24):** Using the same setup as for the preparation of **21**, **11** (60 mg, 0.12 mmol) in 250 mL of methanol (5 × $10^{-4}$ M) was irradiated for 60 min with a 450-W high-pressure mercury lamp. After solvent evaporation, the residue was chromatographed on a short silica gel column. After separation of some oligomers, **24** was collected, 50 mg (83 %), colourless needles, m.p. 215 °C.



**24**

IR (KBr): $\tilde{\nu}$ = 2928 $cm^{-1}$ (s), 2854 (m), 1736 (vs), 1369 (w), 1272 (m), 1235 (m), 1182 (m), 1046 (w). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 6.46 (dd, $J_{7,8} = J_{12,13}$ = 7.7, $J_{7,5} = J_{12,16}$ = 1.5 Hz, 2 H, 7-H, 12-H), 6.23 (d, $J_{5,7} = J_{16,12}$ = 1.5 Hz, 2 H, 5-H, 16-H), 6.20 (d, $J_{8,7} = J_{13,12}$ = 7.7 Hz, 2 H, 8-H, 13-H), 4.40 (br. s, 2 H, 17-H, 26-H), 4.17 (q, $J_{24,25} = J_{33,34}$ = 7.1 Hz, 4 H, 24-H, 33-H), 3.55 (br. s, 2 H, 22-H, 31-H), 3.17–2.91 (m, 14 H, 1a-H, 2a-H, 9-H, 10-H, 18-H, 19-H, 20-H, 21-H, 27-H, 28-H, 29-H, 30-H), 2.60–2.53 (m, 2 H, 1b-H, 2b-H), 1.28 (t, $J_{25,24} = J_{34,33}$ = 7.1 Hz, 6 H, 25-H, 34-H) ppm. $^{13}$C NMR (50.3 MHz, $CDCl_3$): $\delta$ = 172.7 (s, C-23, C-32), 140.6, 139.9, 139.2 (s, C-3, C-4, C-6, C-11, C-14, C-15), 134.6, 132.9, 128.6 (d, C-5, C-7, C-8, C-12, C-13, C-16), 60.7 (t, C-24, C-

Table 2. Crystallographic data for compounds **8**, **12**, and **15**

| Compound | **8**·$CH_2Cl_2$ | **12**·$CH_2Cl_2$ | **15** |
|---|---|---|---|
| Formula | $C_{29}H_{30}Cl_2O_4$ | $C_{33}H_{34}Cl_2O_4$ | $C_{38}H_{40}O_4$ |
| $M_r$ | 513.43 | 565.50 | 560.70 |
| Habit | yellow tablet | orange tablet | red tablet |
| Cryst. size [mm] | 0.6×0.5×0.12 | 0.9×0.5×0.15 | 0.9×0.45×0.18 |
| Crystal system | triclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ | $P2_1/c$ |
| Cell constants: | | | |
| *a* [Å] | 7.5483(10) | 7.7410(12) | 16.983(2) |
| *b* [Å] | 14.498(2) | 41.842(9) | 7.4981(12) |
| *c* [Å] | 23.801(3) | 9.177(2) | 24.724(3) |
| α [°] | 96.011(8) | 90 | 90 |
| β [°] | 93.169(8) | 104.10(2) | 90.039(8) |
| γ [°] | 93.518(10) | 90 | 90 |
| *V* [Å$^3$] | 2580.4 | 2883.0 | 3148.4 |
| *Z* | 4 | 4 | 4 |
| $D_x$ [Mg·m$^{-3}$] | 1.322 | 1.303 | 1.183 |
| $\mu$ [mm$^{-1}$] | 0.29 | 0.26 | 0.08 |
| *F*(000) | 1080 | 1192 | 1200 |
| *T* [°C] | –100 | –130 | –100 |
| $2\theta_{max}$ | 50 | 50 | 50 |
| Refl. measured | 11518 | 6129 | 10829 |
| Refl. indep. | 9038 | 5079 | 5511 |
| $R_{int}$ | 0.025 | 0.027 | 0.045 |
| Parameters | 635 | 354 | 381 |
| Restraints | 577 | 0 | 362 |
| $wR(F^2$, all refl.) | 0.103 | 0.157 | 0.099 |
| $R(F, >4\sigma(F))$ | 0.044 | 0.060 | 0.042 |
| *S* | 0.84 | 1.04 | 0.82 |
| max. Δρ [e·Å$^{-3}$] | 0.40 | 0.58 | 0.15 |

33), 52.1, 48.2, 47.8, 46.1, 42.3, 41.2 (d, C-17, C-18, C-19, C-20, C-21, C-22, C-26, C-27, C-28, C-29, C-30, C-31), 36.1, 32.1 (t, C-1, C-2, C-9, C-10), 14.2 (q, C-25, C-33). MS (70 eV): *m/z* (%) = 508 (5) [$M^+$], 463 (25), 434 (10), 389 (10), 255 (25), 253 (100), 225 (30), 207 (64), 179 (95), 165 (65), 141 (74) ppm. UV (MeOH): $\lambda_{max.}$ (log $\varepsilon$) = 198 nm (4.72), 224 (4.23), 294 (2.94). $C_{34}H_{36}O_4$ (508.70), calcd. C 80.27, H 7.15; found C 80.26, H 7.25.

16. **X-ray Structure Determinations:** Details for compounds **21** and **24** were reported in the preliminary communication.[15] Data collection and reduction: Crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of the diffractometer (**12**: Stoe STADI4; **8, 15**: Siemens P4, with appropriate low-temperature attachments). Measurements were performed with graphite-monochromated Mo-$K_\alpha$ radiation. Structure refinement: The structures were refined anisotropically against $F^2$ (program SHELXL-97, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included with a riding model or rigid methyl groups. For **8** and **15**, displacement parameters were restrained with the commands DELU and SIMU. Details are listed in Table 2. CCDC-246289 (for **8**), -246290 (for **12**), and -246291 (for **15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Data from the preliminary communication[15] were deposited under the numbers CSD-401446 (for **21**), -401447 (for **24**).

## Acknowledgments

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