Synthesis, Structure and Photoreactivity of Several Cinnamophane Vinylogs[‡]

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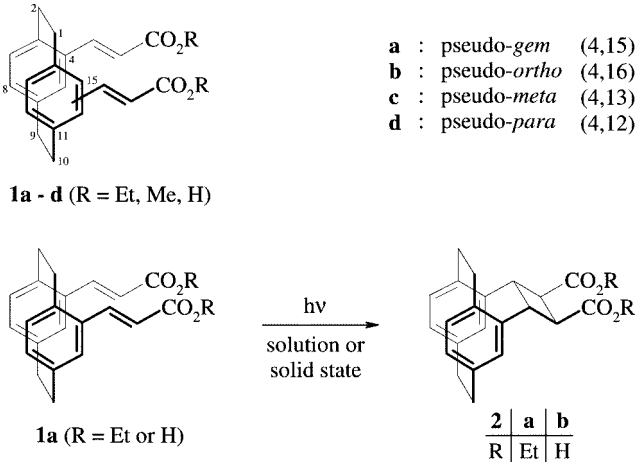
In preceding papers, cinnamophanes **1a–d** (two cinnamic ester units locked in a [2.2]paracyclophane skeleton) were described. In particular, the *pseudo*-gem isomer **1a** was shown to produce in solution an intramolecular cyclobutane photocycloadduct with stereospecificity and very high efficiency, following the topochemical rule observed in the solid state. Here are reported the synthesis and X-ray structure determination of their vinylogs **5a–d**. The photoreactivity of the *pseudo*-gem isomer **5a** was especially investigated in order to examine whether the same specificity would be maintained for the *longer dienic* substituents. It was found that, depending on the irradiation wavelengths, different bicyclic (**8**) and tetracyclic (**9** and **10**) intramolecular photocycloadducts (ladderanes) were produced, but with reduced efficiency as compared to that of **1a**. The pseudo-*ortho*- and pseudo-*para* isomers **5b** and **5d** form the oxetenes **11** and **12**, respectively, on irradiation.

1. Introduction

The [2π + 2π] photocycloaddition of alkenes is a very well documented process.[2–8] In particular, the photoreactivity of cinnamates and related compounds continues to attract great interest.[9–30] Cinnamates are used in various media (solution, molecular assemblies, polymers etc.) for instance as UV screen components[12] or crosslinking agents (photolithography).[9–11] In fluid solutions the major photochemical process is the *cis-trans*-isomerization,[2,3] whereas the competing [2π + 2π] cycloaddition becomes significant when the two reacting centers are close to each other, i.e. in concentrated solutions, in *meso*phases, in tethered bichromophores or in the solid state. In some crystals this is the sole reaction and complete stereocontrol can be achieved according to the *topochemical reaction principle* established by Schmidt and co-workers.[28]



Scheme 1. General structure of cinnamophanes; stereospecific photocycloaddition of **1** with quantitative chemical yield in solution or in the solid state according to refs.[23,24]

In preceding papers,[1,23,24] it was shown that topochemical control could be transferred to fluid solutions when the cinnamic units are locked in a [2.2]paracyclophane skeleton; the resulting compounds were therefore termed "cinnamophanes" (Scheme 1).

Thus, the *pseudo*-gem diester **1a** (R = Et) was found to undergo, in methanol solution, a very efficient (quantum yield ca. 0.8) stereospecific, intramolecular photocycloaddition to **2a** (Scheme 1) in 100 % chemical yield.[23] Similar

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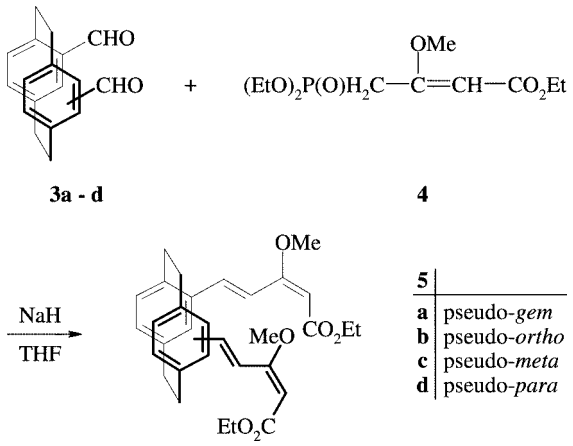
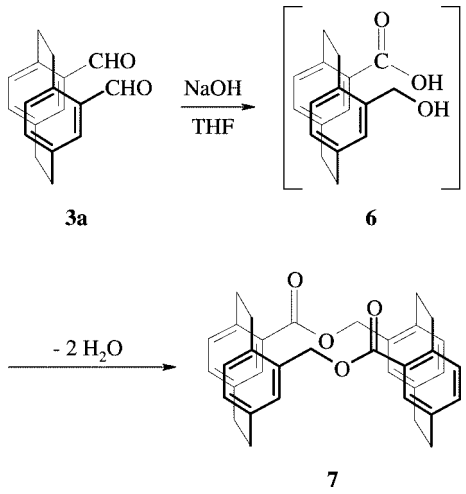


Scheme 2. The preparation of dimethoxy derivatives **5** of vinylogous cinnamophanes



Scheme 3. Formation of the bis(lactone) **7** from the pseudo-*gem* hydroxy acid **6**

results were obtained with the *pseudo*-gem diacid **1a** (R = H),[24] to yield **2b** as also shown in Scheme 1.

The formation of a cyclobutane derivative in **2** induces a significant hypsochromic shift;[23] in an attempt to split **2a** back to **1a** (R = Et), as observed in similar compounds displaying photochromic properties,[4] irradiation was carried out with a low pressure mercury lamp (emitting essentially at 254 nm). Under these conditions the diester **2a** underwent chemical degradation of the cyclophane skeleton as described previously for [2.2]paracyclophane itself.[31] It was considered that this undesirable reaction would be avoided at larger wavelengths, i.e. in a more extended conjugated system. Hence we set out to prepare vinylogous derivatives of **1**.

For synthetic reasons, the methoxy derivatives **5a**–**d** (Scheme 2), incorporating two conjugated double bonds, were investigated first. In this contribution we describe their synthesis, structure determination, spectroscopic, and photochemical properties.

2. Results and Discussion

2.1 Synthesis

The derivatives **5a**–**d** were prepared in one step from the respective dialdehydes **3a**–**d** [32] using a Wittig–Horner reaction with the anion derived from ethyl (*E*)-diethoxyphosphoryl-2-methoxycrotonate (**4**)[33] known to provide *trans*-olefins (Scheme 2).

The yields for the pseudo-*ortho*, -*meta*, and -*para* isomers (**5b**–**d**) were found to be ca. 80 %, whereas the *pseudo*-gem derivative **5a** was isolated in 44 % yield only. One reason for this discrepancy lies in the formation of varying amounts of the side-product **7**, a bis-lactone which could result from the hydroxy acid **6** (Scheme 3). That **3a**, because of the close proximity of its two functional groups, readily undergoes a Cannizzaro-type reaction, has been known for a long time.[34] It appears reasonable to assume that the amount of **6** formed depends on traces of water in the reaction flask. This could hydrolyze the sodium hydride and generate sodium hydroxide, necessary to initiate the disproportionation process of **3a**.

The synthesis of **5a** was not optimized, because a sufficient amount was available to perform the photochemical studies.

The structures of **5a**–**d** were established by the usual spectroscopic and analytical data which are summarized in the Exp. Sect. NMR spectroscopy was of particular importance in determining the stereochemical situation at the double bonds of the cinnamophanes **5**.

Thus, the symmetry in the ^{1}H NMR spectra of all four isomers indicates that both dienic substituents must have the same stereochemistry. The protons at the first double bond next to the paracyclophane core are shifted to low fields (δ = 7.7–7.9 ppm). Their coupling constant (ca. 16 Hz) is typical for a *trans*-configured double bond. The single proton of the second double bond is shifted to higher fields, absorbing in the 5.0–5.2 range. In addition, for three of the four isomers (**5a**, **b**, and **d**) as well as for the interesting lactone **7**, a product type previously not observed in cyclophane chemistry, unambiguous structural evidence was obtained by X-ray structural analysis as described in the following section.

2.2 X-ray Crystal Structures

All single crystals were grown from dichloromethane/ether solution by the vapor-diffusion method; the crystallographic data are summarized in the Exp. Sect.

Derivative **5a** displays a typical [2.2]paracyclophane geometry with the bridgehead carbon atoms C3, C6, C11, and C14 out of the plane of the other ring atoms by 15–17 pm.

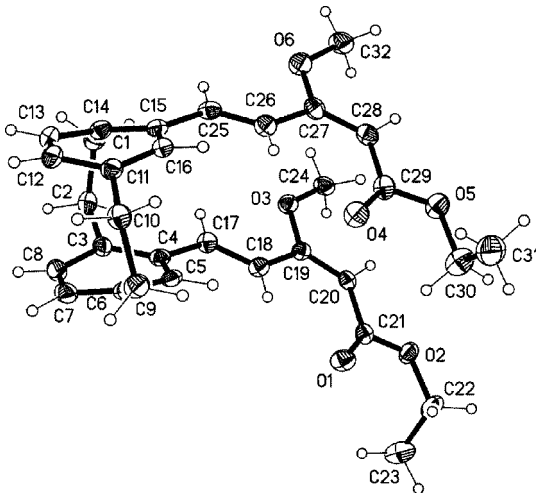


Figure 1. Structure of compound **5a** in the crystal. Ellipsoids represent 30 % probability levels

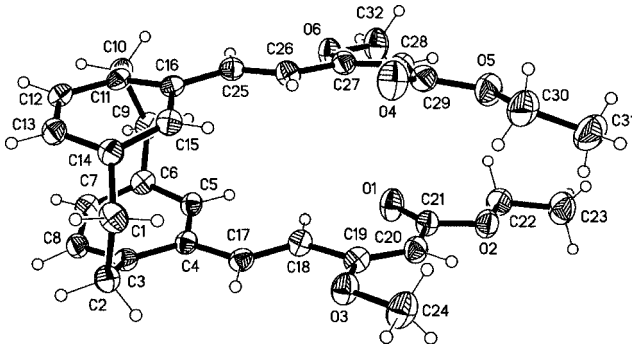


Figure 2. Structure of compound **5b** in the crystal. Ellipsoids represent 30 % probability levels

The distances between the midpoints of the double bonds facing each other amount to ca. 345 and 386 pm, respectively (Figure 1). According to the topochemical rule, they both favor an *intramolecular* [2π + 2π] cycloaddition, in particular the shorter distance, i.e. between C25=C26 and C17=C18.

Diester **5b** displays a pseudo-*ortho* geometry (Figure 2) and intramolecular addition between the double bonds seems unlikely owing to the prohibiting distance between the reacting centers (> 400 pm). However, the proximity (C19···C21: 299 pm) and coplanarity between the carbonyl group (C21/O1) and the double bond (C19/C20) are interesting to note.

The shortest relevant intermolecular distances are C17···C27′: 401 and C18···C28′: 425 pm, respectively, and intermolecular reactions in the solid state should hence not be excluded.

Compound **5d** (Figure 3), which displays crystallographic inversion symmetry, possesses pseudo-*para* geometry, which makes intramolecular coupling between the double bonds impossible. As for **5b**, one observes a short distance also between C11 and O1 (297 pm). The shortest intermolecular

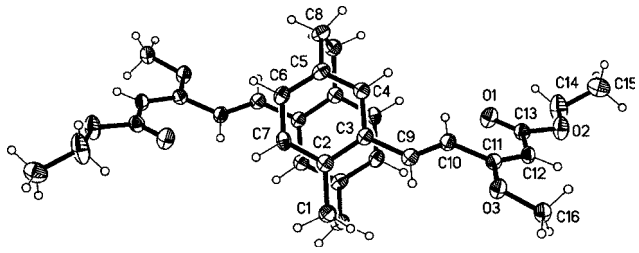


Figure 3. Structure of compound **5d** in the crystal. Ellipsoids represent 30 % probability levels. Only the asymmetric unit is numbered

distance between the two closest double bonds (C11=C12 and C-11′=C-12′) is 392 pm.

Finally, the structure of the *bis*-anhydride **7** is reproduced in Figure 4. It possesses approximate twofold symmetry, but the reliability is reduced by disorder (see X-ray experimental).

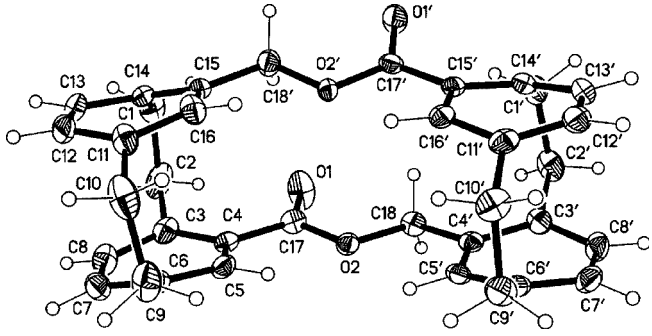


Figure 4. Structure of compound **7** in the crystal. Ellipsoids represent 30% probability levels. The minor disorder component is omitted

2.3 Spectroscopic Studies

Electronic Absorption: The UV absorption spectra of **5a**–**d** in methanol solution are reproduced in Figure 5. Similarly to the four cinnamophane isomers **1a**–**d** (R = Et), compounds **5a**–**d** can be divided into two subgroups: (i) **5a**

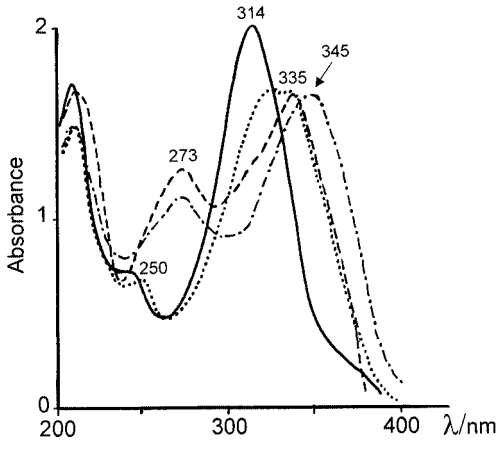


Figure 5. Electronic absorption spectra of **5a**–**d** in methanol (ca. 10^{-5} M); the intensities are not to scale. −−− **5a**; ------ **5b**; ·-·-·- **5c**; ····· **5d**

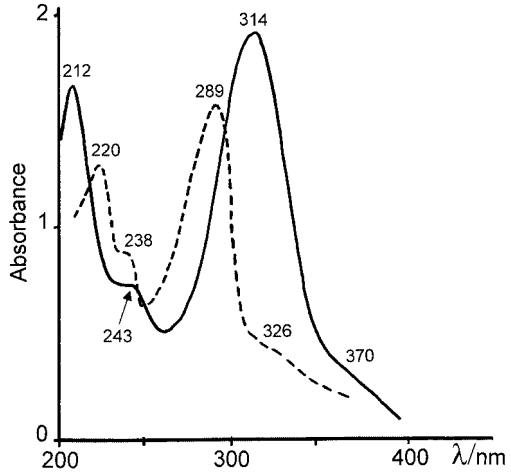


Figure 6. Electronic absorption spectra of pseudo-*gem* derivatives **1a** (------) and **5a** (——) in methanol (10^{-5} M) at ambient temperature. The more intense band undergoes bathochromic shift, $\Delta\tilde{\nu}$ = –2750 cm^{-1} (289–314 nm, $\Delta\lambda$ + 25 nm) and $\Delta\nu$ ca. –3650 cm^{-1} (326–370 nm, $\Delta\lambda$ + 44 nm). The intensities are not to the same scale for **1a** and **5a**

and **5d** in which the substituents form between themselves angles of 0 and 180°, respectively; the partial dipole moments being directed essentially along these directions are assumed to lead to an exciton splitting of the electronic transition.[35] The pseudo-*gem* isomer **5a** shows two absorption maxima at 314 (more intense) and ca. 370 nm (less intense), respectively. (ii) Compounds **5b** and **5c** where the substituents form an angle of ca. 60 and 120° between themselves. These two derivatives display a single intense peak with a maximum at 335 and 345 nm, respectively.

As expected, the UV spectra of **5a–d** are red-shifted as compared to those of **1a–d** (R = Et). Since our main interest in this study concerns the *pseudo*-gem isomer **5a**, a superposition of the UV spectra of **1a** and **5a** is shown in Figure 6. It is noticeable that the more intense band is shifted by ca. 2750 cm^{-1} (289 to 314 nm) and the long wavelength shoulder by ca. 3650 cm^{-1} (326 to 370 nm). Although the empirical tables concerning α,β-unsaturated esters[36] are not meant to apply to strained cyclophanes derivatives, one observes that a double bond extending the conjugation induces an average shift of $\Delta\lambda$ of ca. 30 nm ($\Delta\tilde{\nu}$ ca. 3200 cm^{-1}) in apparent agreement with the tables. However, the methoxy substituent, supposed to induce a further bathochromic shift of 35 nm, has virtually no influence, presumably because it inhibits the coplanarity of the conjugated system.

Fluorescence: Derivatives **5b–d** emit a weak fluorescence (Table 1) with quantum yields about an order of magnitude ($1–5 \times 10^{-3}$) lower than those of **1b–d** (R = Et, $2–6 \times 10^{-2}$);[23,24] those of **5a** and **1a** were found to be less than 10^{-3}. These data are not surprising because diene derivatives provide more deactivating channels than monoolefinic substrates.[37] The spectra are structureless with maxima at ca. 450 to 490 nm. The fluorescence decays were found to be single exponentials and the lifetimes are listed in Table 1, in which the quantum yields and lifetimes of **1a–d** (R = Et) are also listed for comparison (see caption of Table 1).

Table 1. Fluorescence maxima ($\lambda_{max.}$), quantum yields (Φ_F), and lifetimes (τ) of **5a–d** in methanol (10^{-5} M); λ_{exc} = 315 nm at ambient temperature. The quantum yields and lifetimes of **1a–d** are also listed for comparison.

	$\lambda_{max.}$ (nm)	$\Phi_F \times 10^{-3}$		τ (ns)	
Compound	**5**	**5**	**1** (R = Et)	**5**	**1** (R = Et)
a	470	<1	0.6	–	–
b	489	4	30	8.0	15
c	465	<1	20	0.8	15
d	453	5	60	9.9	18

2.4 Photoreactivity

2.4.1 The pseudo-gem Isomer 5a

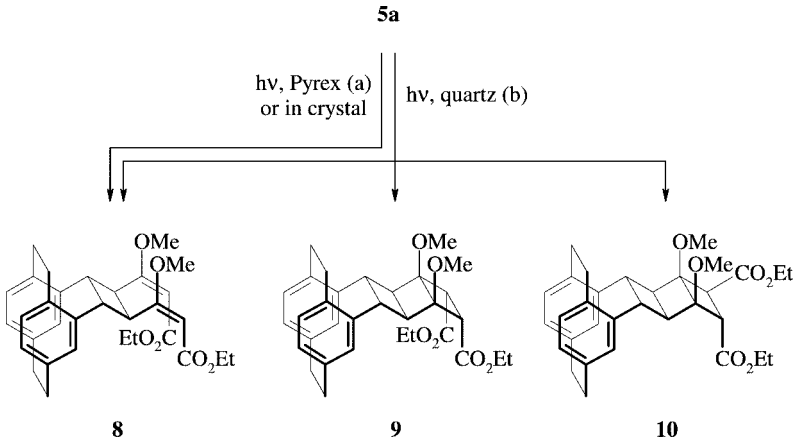
As suggested from the X-ray structure (Section 2.2), compound **5a** is conducive to the formation of intramolecular [2π + 2π] photocycloaddition. Irradiation of an ethanolic solution (10^{-3} M) through Pyrex at ambient temperature was found to lead to the monocycloadduct **8**, isolated in 95 % yield [Scheme 4, conditions (a)].

Compound **8** was characterized by spectrometric methods (Exp. Sect.) and X-ray structural analysis (Figure 7); it crystallizes with two independent but similar molecules (Mol 1: C17–C25: 161.3, C18–C26: 159.5, C19···C27: 295, C20···C28: 388 pm. Mol 2: C17–C25: 162.0, C18–C26: 158.6, C19···C27: 301, C20···C28: 423 pm).

Although the intramolecular distances between the unreacted double bonds of **8** are short enough to allow a second photocycloaddition, this reaction does not take place, presumably because **8** absorbs at much shorter wavelength than **5a**. This is shown in Figure 8 where the UV spectra are recorded as a function of time, during the irradiation at 320 nm.

Under these conditions, **8** was not found to be reactive; in parallel, the quantum yield for the **5a**→**8** conversion, measured at 320 nm, was found to be 0.2. Interestingly, crystals of **5a** (50 mg) in a 1 mm-thick quartz vessel, after irradiation with a 450-W high pressure mercury lamp for 48 h, were found to yield **8** (45 mg) as the sole characterizable product, accompanied by small amounts of oligomeric material [Scheme 4, conditions (a)]. Again, the second potential cyclobutane ring was not formed. Obviously, this photoaddition is too sterically hindered by the solid state environment. Consideration of the X-ray structure of **8** suggests a possible Cope rearrangement (this is the reason why **5a** was irradiated in quartz at low temperature). But **8** was not found to undergo such an isomerization up to 200 °C (DSC analysis), presumably for steric reasons as well.

Using a *quartz filter* [Scheme 4, conditions (b), ethanol] allows absorption in the far UV region, particularly in the band culminating at 230 nm (see Figure 8). The photoproducts were separated by column chromatography into two fractions. The first fraction (41 %) was identified as **10** by



Scheme 4. Intramolecular [2+2] photocycloaddition of **5a** under different conditions

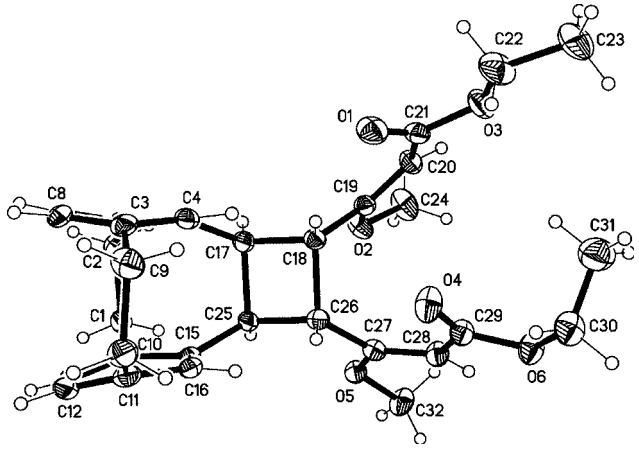


Figure 7. Structure of compound **8** in the crystal. Only one of the two independent molecules is shown. Ellipsoids represent 30 % probability levels

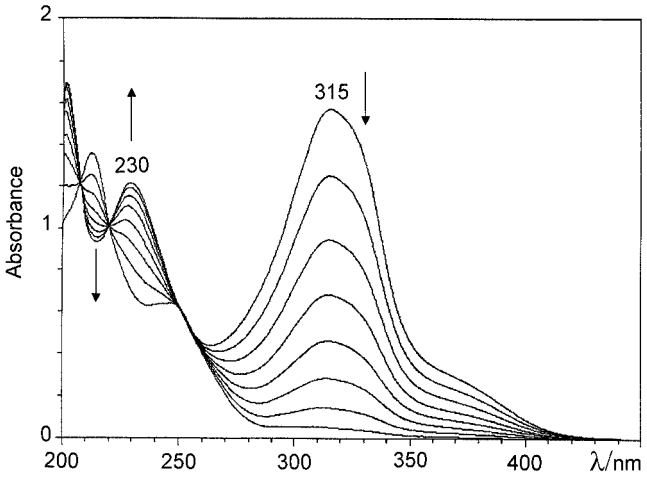


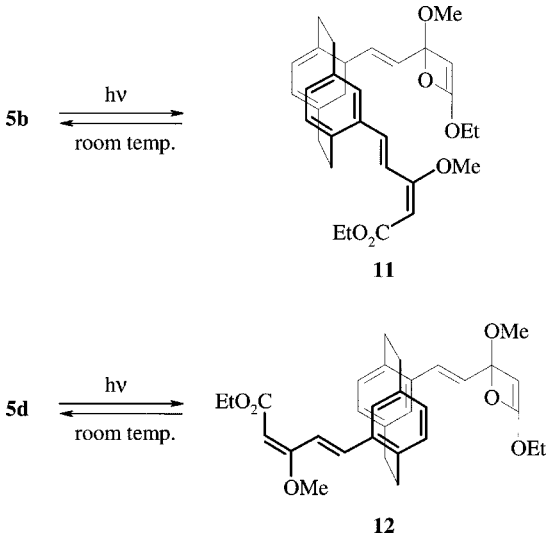
Figure 8. UV spectra of **5a** (10^{-5} M in methanol), upon irradiation at 320 nm, as a function of time; spectra were recorded every 15 s

mass and nmr spectral analysis, and the second to be a mixture (unseparable by chromatography) of **8** and **9**; the latter was characterized by mass spectrometry and nmr (^{1}H, ^{13}C NMR, and COSY correlation, see Exp. Sect.) spectroscopy.[38] In the NMR spectrum of the mixture, the signals of **8** could be subtracted and the remaining signals were attributed to **9**, in accordance with its molecular symmetry (see Exp. Sect.). By integration, the ratio of **9** and **8** in the mixture was determined to be 2:1, the chemical yields amounting to 34 and 17 %, respectively. The total yield of the photoproducts under these conditions is hence 92 %.

It is likely that the formation of **8** by direct irradiation involves the S_1 state in analogy to that of **2a** from **1a** (R = Et).[23,24] The subsequent cyclization may be in competition with *cis-trans* photoisomerization of the second double bond; the nature of the states (S_1 and/or T_1) responsible for the reaction was not investigated. The present results, essentially structural, show that, despite the steric hindrance of head-to-head methoxy groups, the tetracyclic photoproducts **9** and **10** are stable at ambient temperature.

2.4.2 The pseudo-ortho and pseudo-para Isomers 5b and 5d

Irradiation of single crystals of **5b** (50 mg) in a quartz vessel with a 450 W high pressure mercury lamp led to



Scheme 5. Oxetene formation during irradiation of pseudo-*ortho* derivative **5b** and pseudo-*para* derivative **5d**, respectively

oxetene **11** (Scheme 5) as the main photoproduct (5 mg, 10 %), accompanied by traces of several noncharacterized by-products; 35 mg of the starting material was recovered.

The structure of **11** was established by mass spectrometry ([M^+] 516, 45 %) and nmr spectroscopy. The ^{1}H NMR spectrum lacks the symmetry of that of **5b**. New singlets at δ = 4.00 (3 H, OCH_3) and 5.30 (H, ethylenic proton of the oxetene ring) point to the presence of an oxetene derivative. As a chemical proof the slow cycloreversion of **11** back to **5b** can be regarded; this takes place at ambient temperature, as expected.[39] The characterization and isolation at room temperature and after column chromatography of a thermodynamically unstable species such as an oxetene is remarkable. Its formation very likely is facilitated by the proximity and coplanarity of the reacting functional groups (see Figure 2).

Similarly, the *pseudo*-para isomer **5d** produced a small quantity of oxetene **12**, after 1 h of irradiation (Scheme 5); in $CDCl_3$ solution, **5d** was irradiated in an NMR tube and **12** was also characterized by ^{1}H NMR analysis in the mixture of **5d/12**. The thermal back reaction of **12** was monitored by NMR spectroscopy.

Although the photoreactivity of the regioisomers of **5a** was not explored further, it is noteworthy that the main reaction observed in the crystalline state is not *cis-trans*-isomerization (presumably because of lack of free volume due to tight crystal packing) but that of an *unusual cycloaddition* as a result of minimum movement, expected in media of extreme viscosity such as molecular crystals.

3. Conclusion

The synthesis of compound **5a** (in addition to **5b–5d**) was carried out in order to extend the conjugation of previously studied cinnamophanes **1a** that lead very efficiently to [2π + 2 π] photocycloadducts. It was shown that the UV spectrum of **5a** undergoes a significant red-shift, and that irradiation at 320 nm leads to monocycloadduct **8** with a lesser efficiency than **1a** (R = Et) generating **2a**. In ethanol solution in a quartz vessel with a polychromatic lamp, **5a** was found to yield a mixture of **8** and two tetracyclic compounds **9** and **10**. These results provide for the first time some insight into the ladderane formation by intramolecular photoadditions between two parallel unsaturated chains hold in position by a rigid spacer unit (the cyclophane core).[40]

Experimental Section

General: Melting points: Büchi melting point apparatus, uncorrected. TLC: Macherey–Nagel Polygram SilG/UV254 and Polygram Alox N/UV 254. Column chromatography: Merck Kieselgel 60 (70–230 mesh). IR: Perkin–Elmer 1420 and Nicolet 320 FT-IR. NMR: Bruker AM 400.12 MHz (^{1}H) and 100.6 MHz (^{13}C), Bruker AC 200.1 (^{1}H) and 50.3 MHz (^{13}C) and Bruker AC 250.1 (^{1}H) and 62.9 (^{13}C) in $CDCl_3$ and TMS as standard for ^{1}H (δ = 0 ppm) and $CHCl_3$ (δ = 77.05 ppm) for ^{13}C. UV/Vis: Beckman UV 5230 and Hitachi U 3300 using a Mettler UM3 balance (sensitivity 10^{-7} g) for weighing. Fluorescence spectra (corrected for absorption and emission): Hitachi F 4500. Fluorescence quantum yields were determined using quinine sulfate in 1 N H_2SO_4 as external reference (Φ_{FS} = 0.55).[41,42] Fluorescence decays: Applied Physics single photon counting equipment.[1,23,24] The analysis of the fluorescence curves was performed using the DECAN 1.0 programme.[43] All decays observed were found to be single exponentials. Reaction quantum yields were determined as described elsewhere.[44] Irradiations were conducted with high pressure mercury lamps (150 or 450 W). Appropriate filters were employed for selecting regions of the UV emission.[45]

1. **4,15-Bis[(1*E*,3*E*)-4-ethoxycarbonyl-3-methoxybuta-1,3-dienyl]-[2.2]paracyclophane (5a):** NaH (60 % in paraffin oil; 0.64 g, 16 mmol) was suspended in 150 mL of anhydrous THF at 0 °C. Nitrogen was bubbled through the reaction vessel and ethyl (*E*)-diethoxyphosphoryl-2-methoxycrotonate (**4**, 4.7 g, 16.7 mmol) was added slowly. The reaction mixture was stirred at ambient temperature for 45 min. The color changed from slightly yellow to orange and finally became red-brown. Solid 4,15-diformyl[2.2]paracyclophane (**3a**, 0.85 g, 3.2 mmol) was added, and the reaction mixture was stirred for another 30 min at room temp. The reaction was quenched with 100 mL of saturated aqueous NH_4Cl solution, and the layers were separated. The organic phase was concentrated to dryness. The remaining solid was dissolved in CH_2Cl_2, the solution was washed with water twice and dried with $MgSO_4$. The desired product crystallized (yellow rhombs) from CH_2Cl_2 when Et_2O was added. Yield: 0.72 g (1.4 mmol, 44 %). M.p. 162 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 16.0 Hz, 2 H), 7.29 (d, *J* = 16.0 Hz, 2 H), 6.80 (m, 2 H), 6.50 (m, 4 H), 5.02 (s, 2 H), 4.16 (q, *J* = 7.1 Hz, 4 H), 3.70 (s, 6 H), 3.65–3.60 (m, 2 H), 3.10–2.97 (m, 6 H), 1.31 (t, *J* = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.30 (s, 4 C), 139.64 (s, 2 C), 138.99 (s, 2 C), 136.59 (s, 2 C), 134.88 (d, 2 C), 133.60 (d, 2 C), 133.27 (d, 2 C), 130.89 (d, 2 C), 120.57 (d, 2 C), 91.38 (d, 2 C), 59.46 (t, 2 C), 55.21 (q, 2 C), 39.90 (t, 2 C), 33.00 (t, 2 C), 14.48 (q, 2 C) ppm. IR (FT-IR, KBr): $\tilde{\nu}$ = 3082 cm^{-1} (w), 2970 (m), 2935 (m), 2856 (w), 1700 (s), 1630 (s), 1579 (s), 1443 (m), 1379 (m), 1283 (m), 1148 (s), 1135 (s), 1064 (s), 1043 (m). MS (70 eV): *m*/*z* (%) = 516 (32) [M^+], 470 (12), 455 (14), 424 (14), 409 (26), 327 (8), 257 (8), 225 (14), 211 (76), 185 (32), 171 (100), 153 (24), 129 (26), 115 (8). UV (MeOH): $\lambda_{max.}$ (lg ε) = 212 nm (4.55), 243 (4.26, sh), 314 (4.61), 370 (3.89, sh). UV (toluene): $\lambda_{max.}$ (lg ε) = 248 nm (4.28), 313 (4.62), 322 (4.60), 370 (3.91, sh). R_f (CH_2Cl_2) = 0.17. $C_{32}H_{36}O_6$ (516.68): calcd. 74.39, H 7.04; found C 73.95, H 7.04.

2. **4,16-Bis[(1*E*,3*E*)-4-ethoxycarbonyl-3-methoxybuta-1,3-dienyl]-[2.2]paracyclophane (5b):** Same experimental conditions as above. From **3b** (1.0 g, 3.8 mmol) was obtained 1.6 g of **5b** (81 %). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 16.1 Hz, 2 H), 7.31 (d, *J* = 16.1 Hz, 2 H), 6.90 (m, 2 H), 6.50 (m, 4 H), 5.06 (s, 2 H), 4.21–4.00 (m, 4 H), 3.79 (s, 6 H), 3.66–3.60 (m, 2 H), 3.16–3.10 (m, 2 H), 2.97–2.89 (m, 2 H), 2.85–2.78 (m, 2 H), 1.30 (t, *J* = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.09 (s, 2 C), 167.00 (s, 2 C), 139.68 (s, 2 C), 139.19 (s, 2 C), 135.94 (s, 2 C), 135.03 (d, 2 C), 132.85 (d, 2 C), 131.67 (d, 2 C), 128.65 (d, 2 C), 120.22 (d, 2 C), 91.87 (d, 2 C), 59.24 (t, 2 C), 55.39 (q, 2 C), 34.31 (t, 2 C), 33.95 (t, 2 C), 14.39 (q, 2 C) ppm. IR (FT-IR, KBr): $\tilde{\nu}$ = 3087 cm^{-1} (w), 2938 (m), 1706 (s), 1699 (s), 1630 (s), 1440 (m), 1378 (m), 1296 (m), 1284 (s), 1230 (m), 1135 (s), 1069 (s), 1049 (m). MS (70 eV): *m*/*z* (%) = 516 (69) [M^+], 469 (44), 424 (15), 397 (15), 372 (11), 258 (19), 212 (75), 197 (33), 185 (44), 171 (100), 153 (83), 129 (70), 115 (29), 69 (34). UV (MeOH): $\lambda_{max.}$ (lg ε) = 210 nm (4.46), 273 (4.37), 310 (4.38, sh), 335 (4.46). M.p. 158 °C (yellow platelets

from CH_2Cl_2). R_f (CH_2Cl_2) = 0.19. $C_{32}H_{36}O_6$ (516.68): calcd. C 74.39, H 7.04; found C 74.39, H 7.29.

3. **4,13-Bis[(1*E*,3*E*)-4-ethoxycarbonyl-3-methoxybuta-1,3-dienyl]-[2.2]paracyclophane (5c):** Same experimental conditions as above. From **3c** (1.0 g, 3.8 mmol) was obtained 1.6 g of **5c** (81 %). ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 7.91 (d, J = 15.9 Hz, 2 H), 7.33 (d, J = 15.9 Hz, 2 H), 6.80 (d, J = 1.5 Hz, 2 H), 6.61 (d, J = 7.8 Hz, 2 H), 6.43 (dd, J_1 = 7.8, J_2 = 1.5 Hz, 2 H), 5.16 (s, 2 H), 4.22 (q, J = 7.1 Hz, 4 H), 3.78 (s, 6 H), 3.54–3.41 (m, 2 H), 3.14–2.91 (m, 4 H), 2.84–2.71 (m, 2 H), 1.31 (*t*, J = 7.1 Hz, 6 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 167.59 (s, 2 C), 167.23 (s, 2 C), 140.08 (s, 2 C), 139.40 (s, 2 C), 136.78 (s, 2 C), 132.88 (d, 2 C), 132.43 (d, 2 C), 131.70 (d, 2 C), 130.58 (d, 2 C), 120.47 (d, 2 C), 92.13 (d, 2 C), 59.68 (t, 2 C), 55.59 (q, 2 C), 34.87 (t, 2 C), 33.50 (t, 2 C), 14.54 (q, 2 C) ppm. IR (FT-IR, KBr): $\tilde{\nu}$ = 3084 cm^{-1} (w), 2954 (m), 2929 (m), 1699 (s), 1632 (s), 1582 (s), 1378 (m), 1253 (m), 1191 (m), 1146 (s), 1065 (s). MS (70 eV): *m*/*z* (%) = 516 (20) [M$^+$], 471 (14), 455 (12), 442 (10), 409 (24), 257 (8), 211 (80), 185 (30), 171 (100), 153 (30), 129 (36). UV (MeOH): $\lambda_{max.}$ (lg ε) = 210 nm (4.50), 273 (4.36), 345 (4.54). m.p. 176 °C (amorphous powder from CH_2Cl_2). R_f (CH_2Cl_2) = 0.21. $C_{32}H_{36}O_6$ (516.68): calcd. C 74.39, H 7.04; found C 74.47; H 7.16.

4. **4,12-Bis[(1*E*,3*E*)-4-ethoxycarbonyl-3-methoxybuta-1,3-dienyl]-[2.2]paracyclophane (5d):** Same experimental conditions as above. From **3d** (0.5 g, 1.9 mmol) was obtained 0.8 g of **5d** (79 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.88 (d, J = 15.9 Hz, 2 H), 7.39 (d, J = 15.9 Hz, 2 H), 6.75 (d, J = 1.6 Hz, 2 H), 6.61 (dd, J = 7.8, J = 1.6 Hz, 2 H), 6.41 (d, J = 7.8 Hz, 2 H), 5.18 (s, 2 H), 4.21 (q, J = 7.1 Hz, 4 H), 3.82 (s, 6 H), 3.45–3.32 (m, 2 H), 3.10–2.90 (m, 6 H), 1.32 (t, J = 7.1 Hz, 6 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 139.53 (d, 2 C), 133.71 (d, 2 C), 133.22 (d, 2 C), 130.92 (d, 2 C), 120.58 (d, 2 C), 91.99 (d, 2 C), 59.57 (t, 2 C), 55.49 (q, 2 C), 34.38 (t, 2 C), 33.15 (t, 2 C), 14.45 (q, 2 C) ppm. None of the signals of the quaternary C atoms were observed due to the poor solubility of the compound. IR (FT-IR, KBr): $\tilde{\nu}$ = 3088 cm^{-1} (w), 2978 (w), 2935 (m), 1690 (s), 1631 (s), 1577 (s), 1443 (m), 1378 (m), 1280 (s), 1192 (s), 1147 (s), 1061 (s), 1042 (s). MS (70 eV): *m*/*z* (%) = 516 (100) [M$^+$], 470 (46), 424 (34), 397 (24), 372 (22), 299 (18), 258 (18), 213 (70), 212 (70), 211 (60), 197 (34), 171 (76), 153 (40), 129 (38), 71 (16). UV (MeOH): $\lambda_{max.}$ (lg ε) = 210 nm (4.19), 250 (3.84), 322 (4.24), 334 (4.24). M.p. 232 °C (colorless platelets from CH_2Cl_2). R_f (CH_2Cl_2) = 0.23. $C_{32}H_{36}O_6$ (516.68): calcd. C 74.39, H 7.04; found C 74.16, H 7.14.

5. **Irradiation of 4,15-Bis[(1*E*,3*E*)-4-ethoxycarbonyl-3-methoxybuta-1,3-dienyl][2.2]paracyclophane (5a) in Ethanol: 5a** (100 mg, 0.19 mmol) was dissolved in 250 mL of ethanol and the solution irradiated with a 150-W high-pressure mercury light source (Pyrex glass) for 30 min, while nitrogen was bubbled through the solution. For work-up the solvent was removed by evaporation and the residue recrystallized from CH_2Cl_2/Et_2O. The photoaddition product **8** was isolated as a colorless solid in 95 % yield (0.95 g). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 6.52 (d, J = 1.5 Hz, 2 H), 6.47 (dd, J_1 = 7.7, J_2 = 1.5 Hz, 2 H), 6.21 (d, J = 7.7 Hz, 2 H), 5.41 (m, 2 H), 5.01 (s, 2 H), 4.73–4.72 (m, 2 H), 4.12 (q, J = 7.1 Hz, 4 H), 3.71 (s, 6 H), 3.23–3.18 (m, 4 H), 3.02–2.98 (m, 2 H), 2.59–2.55 (m, 2 H), 1.28 (t, J = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 173.12 (s, 2 C), 166.80 (s, 2 C), 140.36 (s, 2 C), 139.47 (s, 2 C), 139.37 (s, 2 C), 134.37 (d, 2 C), 133.13 (d, 2 C), 128.73 (d, 2 C), 91.62 (d, 2 C), 59.36 (t, 2 C), 55.59 (q, 2 C), 44.09 (d, 2 C), 38.01 (d, 2 C), 36.32 (t, 2 C), 32.52 (t, 2 C), 14.41 (q, 2 C) ppm. IR (FT-IR, KBr): $\tilde{\nu}$ = 3084 cm^{-1} (w), 2974 (m), 2936 (m), 1712 (s), 1624 (s), 1380 (m), 1244 (m), 1191 (s), 1147 (s), 1140 (s), 1067 (s). MS (70 eV): *m*/*z* (%) = 516 (28) [M$^+$], 471 (16), 455 (15), 424 (16), 409 (24), 257 (10), 225 (12), 211 (80), 185 (28), 171 (100), 153 (26), 129 (30). UV (MeOH): $\lambda_{max.}$ (lg ε) = 228 nm (4.18), 292 (3.17). m.p.: 201 °C (colorless crystals from CH_2Cl_2). R_f (CH_2Cl_2) = 0.19. $C_{32}H_{36}O_6$ (516.68): calcd. C 74.39, H 7.04; found C 74.42, H 7.09.

6. **Irradiation of 4,15-Bis[(1*E*,3*E*)-4-ethoxycarbonyl-3-methoxybuta-1,3-dienyl][2.2]paracyclophane (5a) at –30 °C in Quartz Glass: 5a** (150 mg, 0.29 mmol) was dissolved in 250 mL of ethanol and the solution irradiated with a 150-W high-pressure mercury light source for 30 min. The quartz glass irradiation vessel was immersed into a –30 °C cold bath and nitrogen was bubbled through the solution during the reaction. For work-up the solvent was removed by evaporation under vacuum (water bath, 60 °C). Silica gel chromatography of the residue with petroleum ether, CH_2Cl_2, and Et_2O (11:7:1) provided two fractions: Fraction 1: unsymmetrical [3]ladderane **10**, 60 mg (41 %); Fraction 2: 1:2 mixture of starting material **5a** and symmetrical [3]ladderane **9**, 80 mg (52 %). **Unsymmetrical [3]Ladderane 10:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 6.47 (br. d, J = 7.8 Hz, 2 H), 6.27 (br. s, 1 H), 6.22 (d, J = 7.8 Hz, 1 H), 6.21 (d, J = 7.8 Hz, 1 H), 6.20 (br. s, 1 H), 4.54 (br. s, 2 H), 4.38 (d, J = 6.9 Hz, 1 H), 4.31–4.23 (m, 2 H), 4.20 (q, J = 7.1 Hz, 2 H), 3.67 (d, J = 6.9 Hz, 1 H), 3.53 (s, 3 H), 3.36–3.35 (m, 1 H), 3.24 (s, 3 H), 3.19–2.93 (m, 7 H), 2.59–2.54 (m, 2 H), 1.32 (t, J = 7.1 Hz, 3 H), 1.24 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 171.08 (s, 1 C), 170.22 (s, 1 C), 140.08 (s, 1 C), 140.04 (s, 1 C), 139.81 (s, 1 C), 139.76 (s, 1 C), 139.73 (s, 1 C), 139.46 (s, 1 C), 134.64 (d, 1 C), 134.45 (d, 1 C), 133.20 (d, 1 C), 132.84 (d, 1 C), 128.66 (d, 1 C), 84.12 (s, 1 C), 83.15 (s, 1 C), 61.33 (t, 1 C), 61.02 (t, 1 C), 52.62 (q, 1 C), 52.24 (q, 1 C), 47.28 (d, 1 C), 45.60 (d, 1 C), 43.58 (d, 1 C), 42.70 (d, 1 C), 40.85 (d, 1 C), 36.65 (d, 1 C), 36.10 (t, 1 C), 36.01 (t, 1 C), 32.46 (t, 1 C), 31.69 (t, 1 C), 14.28 (q, 1 C), 14.12 (q, 1 C). IR (FT-IR, KBr): $\tilde{\nu}$ = 3083 cm^{-1} (w), 2939 (m), 2839 (w), 1726 (s), 1307 (s), 1274 (s), 1213 (s), 1194 (s), 1032 (s). MS (70 eV): *m*/*z* (%) = 516 (20) [M$^+$], 501 (10), 470 (16), 455 (18), 442 (15), 424 (16), 409 (38), 379 (15), 365 (10), 327 (8), 225 (12), 211 (76), 197 (14), 185 (24), 171 (100), 153 (20), 129 (22). UV (CH_3CN): λ_{max} (lg ε) = 222 nm (4.26), 262 (3.23, sh). M.p. 149 °C (colorless rhombic crystals from CH_2Cl_2). R_f (petroleum ether ether: CH_2Cl_2/Et_2O, 11:7:1) = 0.50. $C_{32}H_{36}O_6$ (516.68): calcd. C 74.39, H 7.04; found C 74.24, H 7.21. **Symmetrical [3]Ladderane 9:** [38] ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 6.47 (dd, J_1 = 7.8, J_2 = 1.6 Hz, 2 H), 6.27 (d, J = 1.6 Hz, 2 H), 6.22 (d, J = 7.8 Hz, 2 H), 4.58 (br. s, 2 H), 4.23 (q, J = 7.1 Hz, 4 H), 3.87 (s, 2 H), 3.54 (br. s, 2 H), 3.25 (s, 6 H), 3.23–3.12 (m, 4 H), 3.03–2.98 (m, 2 H), 2.60–2.54 (m, 2 H), 1.29 (t, J = 7.1 Hz, 6 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 170.17 (s, 2 C), 140.12 (s, 2 C), 139.91 (s, 2 C), 139.82 (s, 2 C), 134.89 (d, 2 C), 133.03 (d, 2 C), 128.81 (d, 2 C), 81.76 (s, 2 C), 60.74 (t, 2 C), 51.47 (q, 2 C), 45.54 (d, 2 C), 43.20 (d, 2 C), 36.33 (d, 2 C), 36.10 (t, 2 C), 32.18 (t, 2 C), 14.36 (q, 2 C) ppm. All values were obtained by subtracting the signals for the unsymmetrical [3]ladderane from the composite spectrum.

7. **Irradiation of 4,16-Bis[(1*E*,3*E*)-4-ethoxycarbonyl-3-methoxybuta-1,3-dienyl][2.2]paracyclophane (5b) in the Solid State:** Single crystals of 4,16-bis[(1*E*,3*E*)-4-ethoxycarbonyl-3-methoxybuta-1,3-dienyl]-[2.2]paracyclophane (**5b**, 50 mg) were placed in a quartz glass cell (thickness: 1 m) and irradiated with a 450-W mercury high pressure lamp for 24 h. The color of the crystals changed from slightly yellow to slightly brown. The crystals were dissolved in CH_2Cl_2, a thin insoluble residue remaining on the surface of the quartz cell facing the light source. Silica gel chromatography of the solution with CH_2Cl_2 provided starting material **5b** (35 mg) and the oxetene **11**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.89 (d, J = 16.0 Hz, 1 H), 7.31 (d, J = 16.0 Hz, 1 H), 7.19 (d, J = 15.7 Hz, 1 H), 6.87 (m, 1 H),

Table 2. Crystallographic data for compounds **5a**, **5b**, **5d**, **7**, and **8**

Compound	**5a**	**5b**	**5d**	**7**	**8**
Formula	$C_{32}H_{36}O_6$	$C_{32}H_{36}O_6$	$C_{32}H_{36}O_6$	$C_{36}H_{32}O_4$	$C_{32}H_{36}O_6$
M_r	516.61	516.61	516.61	528.62	516.61
Habit	yellow tablet	colourless tablet	colourless block	colourless prism	colourless plate
Crystal size (mm)	0.4×0.4×0.2	0.4×0.4×0.18	0.4×0.4×0.3	0.34×0.3×0.25	0.6×0.3×0.12
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	P	$P2_1/n$	$P2_1/c$
Cell constants:					
a (Å)	8.408(2)	26.928(7)	7.487(4)	11.863(5)	11.533(5)
b (Å)	14.794(4)	8.654(3)	8.542(4)	13.106(6)	33.692(12)
c (Å)	21.731(4)	24.680(7)	11.600(5)	16.795(6)	13.987(5)
α (°)	90	90	68.65(4)	90	90
β (°)	94.13(2)	103.88(3)	87.18(4)	96.42(5)	90.60(3)
γ (°)	90	90	72.73(4)	90	90
V (Å^3)	2696.1	5583	658.4	2595	5435
Z	4	8	1	4	8
D_x (Mg·m^{-3})	1.273	1.229	1.303	1.353	1.263
M (mm^{-1})	0.09	0.08	0.09	0.09	0.09
F(000)	1104	2208	276	1120	2208
T (°C)	–130	–70	–100	–130	–100
$2\theta_{max.}$	50	50	50	50	50
Refl. measured	5419	6437	2599	6194	10118
Refl. indep.	4724	4942	2315	4578	9558
R_{int}	0.123	0.054	0.060	0.027	0.080
Parameters	347	347	174	394	693
Restraints	332	353	157	552	805
$wR(F^2$, all refl.)	0.202	0.196	0.223	0.169	0.211
$R[F, >4\sigma(F)]$	0.073	0.058	0.064	0.065	0.063
S	1.04	0.95	0.98	1.06	0.98
max. Δρ (e·Å^{-3})	0.44	0.30	0.31	0.24	0.28

6.73 (m, 1 H), 6.53 (m, 2 H), 6.51 (m, 2 H), 6.27 (d, J = 15.7 Hz, 1 H), 5.30 (m, 1 H), 5.18 (s, 1 H), 4.22–4.09 (m, 4 H), 4.00 (s, 3 H), 3.83 (s, 3 H), 3.74–2.83 (m, 8 H), 1.30 (t, J = 7.1 Hz, 3 H), 1.27 (t, J = 7.1 Hz, 3 H) ppm. MS (70 eV): m/z (%) = 516 (42) [M$^+$], 470 (34), 424 (14), 397 (22), 372 (18), 299 (18), 211 (68), 185 (46), 171 (100), 153 (66), 129 (72). m.p. 40–45 °C. R_f (CH_2Cl_2) = 0.07.

8. **Irradiation of 4,12-Bis[(1*E*,3*E*)-4-ethoxycarbonyl-3-methoxybuta-1,3-dienyl][2.2]paracyclophane (5d) in Solution:** A solution of **5d** in $CDCl_3$ (2–3 mg per 1 mL) was irradiated with monochromatic light (366 nm) for 1 h in a NMR quartz glass tube. A ^{1}H NMR spectrum measured immediately after the irradiation showed two new signals indicative of the oxetene **12**: δ = 5.19 (probably oxetene proton) and δ = 4.4 ppm (CH_3 protons of the methoxy group at the oxetene ring). Furthermore, the NMR spectrum became more complicated, especially in the aromatic range (δ = 6.80–6.30 ppm). The intensity of the vinyl protons diminished. After the sample had been stored for 48 h in the dark, ^{1}H NMR analysis no longer showed these signals. Rather, the NMR spectrum of the starting material **5d** (before irradiation) was registered.

9. **X-ray Structure Determinations. Data Collection and Reduction:** Crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of the diffractometer (**5a**,**7**: Stoe STADI-4; **5b, 5d, 8**: Siemens P4, with appropriate low temperature attachments). Measurements were performed with graphite-monochromated Mo-K_α 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. Because of the generally moderate crystal quality, displacement parameters were restrained with the commands DELU and SIMU to improve stability of refinement. In compound **7**, the chains C17(=O1)–O2–C18 and C17′(=O1′)–O2′–C18′ are disordered, whereby their antiparallel counterparts are occupied to the extent of 14.2(5)%. Appropriate similarity restraints were applied. Crystallographic data for compounds **5a**, **5b**, **5d**, **7**, and **8** are collected in Table 2. CCDC-243747 (for **5a**), -243748 (for **5b**), -243749 (for **5d**), -245428 (for **7**) and -243750 (for **8**) 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.

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