

Photochemical Generation of Cyclophanes from 1,3,5-Trisubstituted Benzenes with Chalcone Chromophores

Elena Karpuk,^[a] Dieter Schollmeyer,^[a] and Herbert Meier*^[a]

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(*E,E,E*)-1,3,5-Tricinnamoylbenzene (**7a**) photodimerizes in solution to the [4.4.4](1,3,5)cyclophane **8a**. The process consists of three consecutive steps in which *cisoid* enone conformations of **7a** react in regio- and stereoselective *anti*-head-to-head cycloadditions. (*E,E,E*)-1,3,5-Tris(3-oxo-3-phenylpropenyl)benzene (**13a**), an isomer of **7** with reversed enone units, shows a single [2 π +2 π] cycloaddition of the same type. Due to steric reasons, it is afterwards not capable of intramolecular processes and oligomerizes by intermolecular photo-

cycloadditions. Photolyses in the crystalline state yield dimers by topochemically controlled *syn*-head-to-tail processes (**7a** $\rightarrow$ **10a**, **13a** $\rightarrow$ **15a**). An efficient dimerization of **13a** takes place, although the distance between the olefin centers exceeds with 5.07 Å by far the limit postulated in Schmidt's rule.

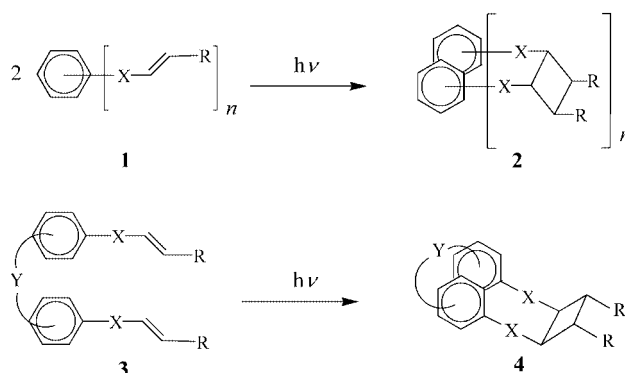
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Introduction

Since the synthesis of [2.2](1,4)cyclophane by Brown and Farthing^[1] in 1949 and the pioneering work of Cram^[2] in the early 1950s, cyclophanes represent a highly attractive class of compounds.^[3] Many different synthetic routes were developed for this purpose. More than 30 years ago, we described the first applications of photocycloaddition reactions for the generation of cyclophanes.^[4,5] In the meantime, various polyfunctional compounds with vinyl, styryl, cinnamoyl or other groups, suitable for [2 π +2 π] cycloadditions, were used.^[3,6] Scheme 1 shows such inter- and intramolecular photocycloaddition reactions with R = H, C₆H₅, COOR and *n* = 2, 3, 4. For X = nil, [2_n]cyclophanes are formed (**1** $\rightarrow$ **2**), while [4_n] and higher systems require X = O, CO, etc.^[3] Phanes having “decks” other than benzene, can be prepared in the same way.

A special aspect of these photoreactions is due to the fact that normally only (*E*)-configurations react,^[7] but they can react in different conformations to different stereoisomers. Conformational selectivities are very rare in organic reactions. Whereas the regiochemistry of the cycloaddition **3** $\rightarrow$ **4** is normally fixed by the molecular architecture of **3**, cyclodimerizations of **1** can follow a head-to-head or a head-to-tail arrangement.

We started now to study the cyclophane formation of benzene derivatives which have in 1,3,5-position cinnamoyl groups (chalcone substructures with X = CO and R = C₆H₅).^[8,9] Different regio- and stereoselective dimerizations



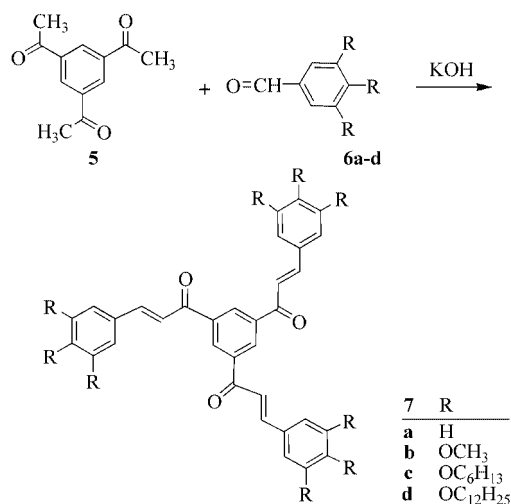
Scheme 1. Inter- and intramolecular [2 π +2 π] photocycloaddition reactions for the formation of cyclophanes.

in the sense of threefold [2 π +2 π] photocycloaddition reactions should result in (1,3,5)cyclophanes with 4 or 5 carbon atoms in the three bridges – depending on head-to-head or head-to-tail additions.

Results and Discussion

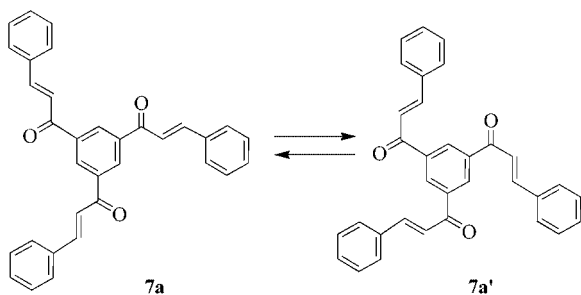
1,3,5-Tricinnamoylbenzenes **7a–d** are easily accessible by alkaline condensation reactions of 1,3,5-triacetylbenzene (**5**) and benzaldehydes **6a–d** (Scheme 2). The parent compound **7a** was obtained in a yield of 70%.^[10,11] Electron-donating substituents in the benzaldehyde components **6** reduce the electrophilicity of the carbonyl carbon atom and consequently decrease the yield (18% for **7c** and 30% for **7d**). A detailed study of the condensation was performed for **5** and **6b**. The ratio **5/6b** of 1:5 led in aqueous ethanolic NaOH at 40 °C after 5 h to a mixture of mono- (25%), di- (20%) and tricondensation product (**7b**, 3%).

[a] Institut für Organische Chemie der Johannes Gutenberg-Universität,
Duesbergweg 10–14, 55099 Mainz, Germany
Fax: +49-6131-3925396
E-mail: hmeier@mail.uni-mainz.de



Scheme 2. Preparation of all-(*E*)-1,3,5-tricinnamoylbenzenes **7a–d**.

Purification of the reaction products by column chromatography/crystallization yields the all-(*E*) configurations of **7a–d**. The three enone units can have *cisoid* or *transoid* conformations. Scheme 3 demonstrates the equilibrium between the all-*cisoid* form **7a** and the all-*transoid* form **7a'**. According to NOE measurements, *cisoid* conformations are preferred. The conformational selectivity, mentioned before for the photocyclodimerization reactions, is a decisive point for the cyclophane formation.



Scheme 3. all-*cisoid* and all-*transoid* conformation of (*E,E,E*)-1,3,5-tris(3-phenylpropenyl)benzene (**7a/7a'**).

Upon irradiation ($\lambda \geq 290$ nm) in solution (2.9×10^{-2} M in CD₂Cl₂, $\lambda_{\text{max}} = 326$ nm, $\epsilon_{\text{max}} = 69040$ cm² mol⁻¹) the parent compound (*E,E,E*)-**7a** reaches soon a photostationary state. The ratio (*E,E,E*)/(*E,E,Z*)/(*E,Z,Z*)/(*Z,Z,Z*), determined by ¹H NMR spectroscopy, amounts to 2.4:8:5. Protonation of the isomeric mixture catalyzes the reverse reaction to all-(*E*)-**7a** so that (*Z*) conformations are below the detection limit of about 3% in the ¹H NMR spectrum.

Irradiation of **7a** in more concentrated solutions (14×10^{-2} M in CH₂Cl₂) yields 81% of a dimer **8a** which contains three four-membered rings in an arrangement with a C₃ axis. The process is highly selective since no other dimers can be found. The remaining 19% are monomer and small amounts of polymer.

Scheme 4 shows the five possible structures for **8a**. The photodimerization occurs probably via an excimer whose geometry may be independent of the preferred *cisoid* con-

formations in the ground state, but certainly contains only *trans*-configured double bonds. The structures **8aa**, **8ab** and **8ac** represent [4.4.4](1,3,5)cyclophanes which can be generated in threefold head-to-head *syn* or *anti* photocycloadditions: **8aa** from **7a'** + **7a'** with *cis* arrangement of the heads (and tails); **8ab** from **7a** + **7a** with *trans* arrangement of the heads; **8ac** from **7a** + **7a** with *cis* arrangement of the heads.

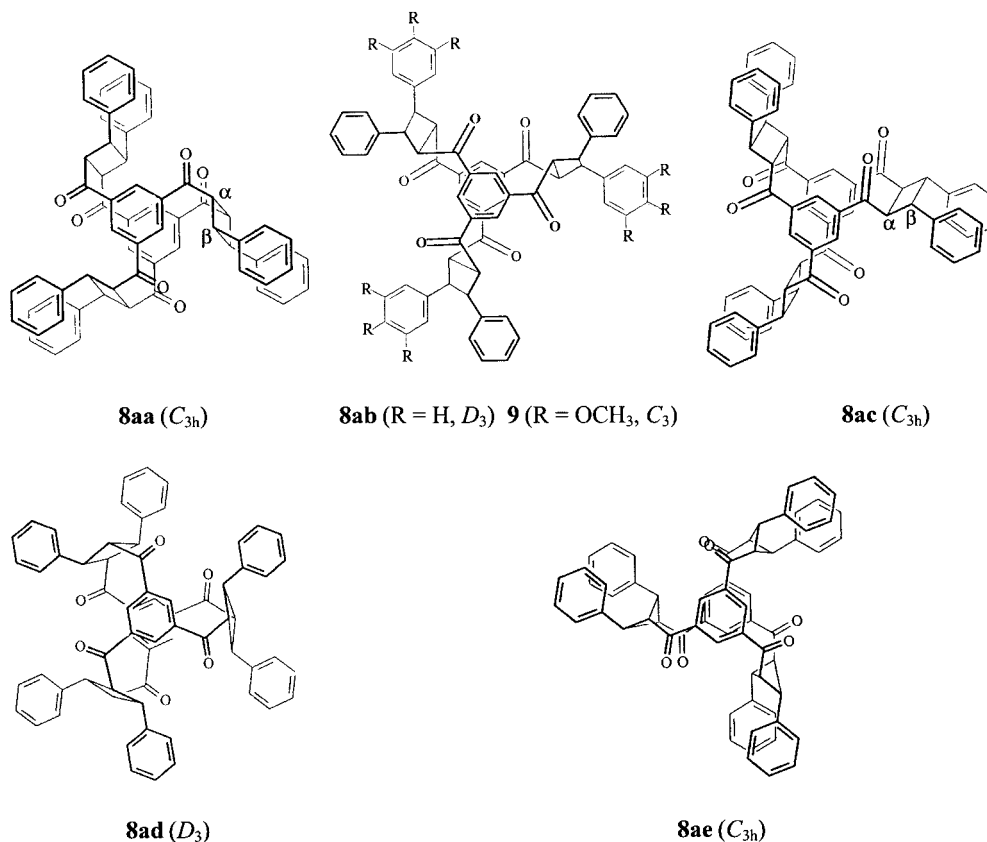
The structures **8ad** and **8ae** represent [5.5.5](1,3,5)cyclophanes which can be generated in threefold head-to-tail photocycloadditions: **8ad** from **7a'** + **7a'** with *cis* arrangement of the heads; **8ae** from a mixed addition **7a** + **7a'** with *cis* arrangement of the heads.

All other thinkable arrangements are too strained to permit three consecutive [2 π +2 π] processes. Nevertheless, the differentiation between the five isomers **8aa–8ae** turned out to be very difficult.

The four-membered ring protons in **8aa**, **8ab** and **8ac** should give rise to AA'BB' spin patterns in the ¹H NMR spectra; **8ad** should give an A₂B₂ spin pattern and **8ae** an ABC₂ system which is converted by molecular dynamics, which is fast in terms of the NMR time scale, to an A₂B₂ system. The observed spin pattern is not in accordance with A₂B₂ or ABC₂ systems. Therefore, the head-to-tail adducts **8ad** and **8ae** can be ruled out. Calculation of the observed AA'BB' spin pattern^[13] rendered the parameters listed in Table 1 for **8a**. NOE measurements showed a positive effect for the neighborhood of the protons on the central benzene ring ($\delta = 7.81$ ppm) and the α -protons of the four-membered rings ($\delta = 3.90$ ppm), but not for the β -protons ($\delta = 4.47$ ppm). Consequently, structure **8aa** can be eliminated. The final differentiation between **8ab** and **8ac** proved to be very complex since neither through-bond connectivity (H,H coupling)^[14] nor through-space connectivity (NOE) allowed a clear decision. Ultimately, we succeeded with a mixed cycloadduct. Irradiation of **7a/7b** (ratio 2:1) yielded traces of **8a**, the dimer **8b** as a byproduct and the mixed cycloadduct **9** (Scheme 4) as major component. The statistical ratio **8a/8b/9** would be 4:1:4; the experimental ratio was $\leq 4:19:77$ which proves the higher reactivity of **7b** compared to **7a**. The four-membered ring protons of the mixed adduct **9** have an ABCD spin pattern, and NOE measurements showed that the C₃ structure of **9**, which corresponds to the D₃ structure **8ab** is correct. Irradiation of the singlet of the protons on the trimethoxybenzene ring ($\delta = 6.63$ ppm) resulted in positive NOEs for both β -protons on the four-membered rings ($\delta = 4.37, 4.49$ ppm); that means the terminal benzene rings must have the *trans* arrangement present in **8ab** and formula **8ac** can be rejected. Irradiation of the pure monomers **7b–d** yields [4.4.4](1,3,5)cyclophanes whose structures correspond to **8ab**.^[15]

The photochemical cyclophane formation **7** $\rightarrow$ **8** can be summarized as follows: *cisoid* (*E*) configurations of **7** react in three consecutive steps in a regioselective head-to-head mode, and in a stereoselective way, so that vicinal protons on the four-membered rings have always *trans* arrangement.

Irradiation of **7a** in the crystalline state yields a dimer **10a** which contains only one four-membered ring



Scheme 4. Possible isomeric [4.4.4](1,3,5)- and [5.5.5](1,3,5)cyclophanes **8** obtained by threefold photocycloaddition reactions of **7a** and mixed cycloadduct **9** obtained from **7a** and **7b**.

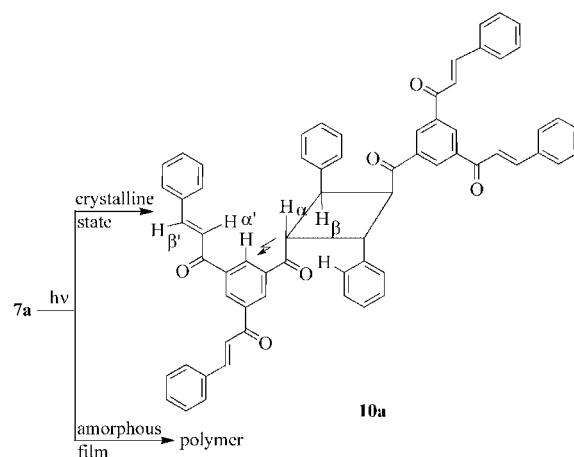
Table 1. ^1H NMR chemical shifts (δ values in ppm, measured in CDCl_3 , TMS as internal standard) and calculated^[13] coupling constants (absolute values in Hz) of the four-membered ring protons which generate AA'BB' spin patterns in **8a**, **10a**, **14a** and **15a**.

Compd.	Cycloadd. type	δ (A) [a]	δ (B) [a]	J (AA')	J (AB)	J (AB')	J (BB')
8a	h-to-h <i>anti</i>	4.47	3.90	9.95	8.95	0.25	9.95
10a	h-to-t <i>syn</i>	5.16	4.94	0.85	10.75	6.85	0.90
14a	h-to-h <i>anti</i>	4.66	4.15	9.60	8.80	0.25	9.60
15a	h-to-t <i>syn</i>	5.07	4.95	0.85	10.75	6.85	0.90

[a] The protons A with signals at lower field are on the side of the phenyl substituents, the protons B on the carbonyl side.

(Scheme 5). The structure determination of **10a** is based on one- and two-dimensional NMR studies. Irradiation of the signal of the aromatic protons ($\delta = 8.47$ ppm) on the central benzene ring leads to NOEs for the four-membered ring protons H_α ($\delta = 4.94$ ppm), H_β ($\delta = 5.16$ ppm), the olefinic protons $H_{\alpha'}$ ($\delta = 7.52$ ppm), $H_{\beta'}$ ($\delta = 7.87$ ppm) and the *ortho*-proton ($\delta = 7.30$ ppm) of the phenyl group (Scheme 5). This result proves the head-to-tail regioselectivity and the stereoselective *syn*-[2 π +2 π] photocycloaddition reaction. Other dimers could not be found. Apart from 66% of **10a**, only monomer **7a** (34%) was obtained. The

topochemically controlled photodimerization comes to an end when the crystal lattice breaks down.



Scheme 5. Photochemistry of **3a** in the crystalline state and in an amorphous film.

The protons on the four-membered ring exhibit an AA'BB' spin pattern according to the C_i symmetry of **10a**; comparison with the corresponding data of **8ab** reveals higher δ values for **10a**, because the second aromatic "deck" is not present in **10a**. Additionally, a 3J (*cis*) coupling of 6.85 Hz was found for **10a** which is smaller than the 3J (*trans*) couplings in **8ab** (Table 1).

Figure 1 shows the reaction spectra of the irradiation of a spin-coated film of **7a**. The long-wavelength absorption causes a broader and somewhat bathochromically shifted band ($\lambda_{\text{max}} = 331 \text{ nm}$) in the amorphous state. Monochromatic irradiation with $\lambda = 366 \text{ nm}$ leads to a complete disappearance of the band. The film becomes totally insoluble in organic solvents. The chalcone chromophores enter in this aggregated but not really ordered state photopolymerization and photocrosslinking reactions in which finally all enone building blocks are involved.

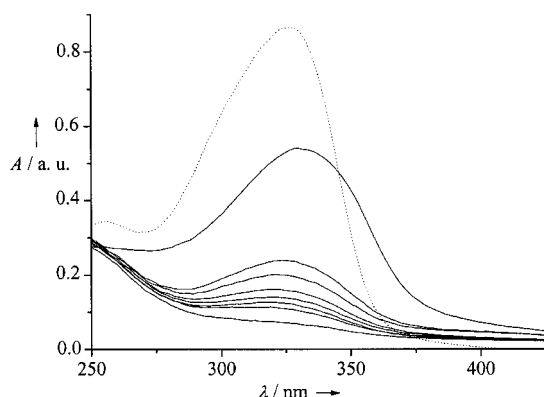
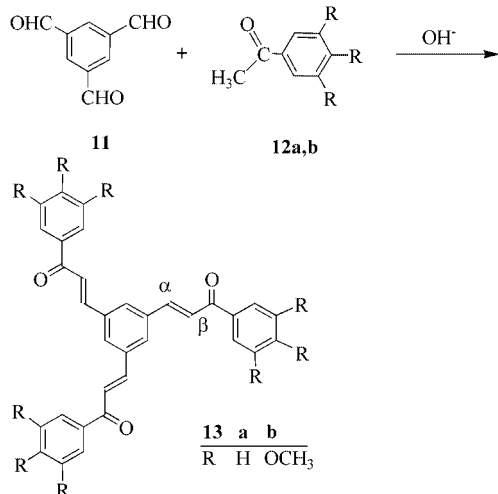


Figure 1. Time-resolved UV/Vis spectra (absorbance A) of the monochromatic ($\lambda = 366 \text{ nm}$) irradiation of a spin-coated film of **7a**. Measurement after 0, 15, 30, 45, 60, 75, 165 and 465 s (top to bottom). The dotted line corresponds to the spectrum measured for a $1.03 \times 10^{-4} \text{ M}$ solution in CH_2Cl_2 .

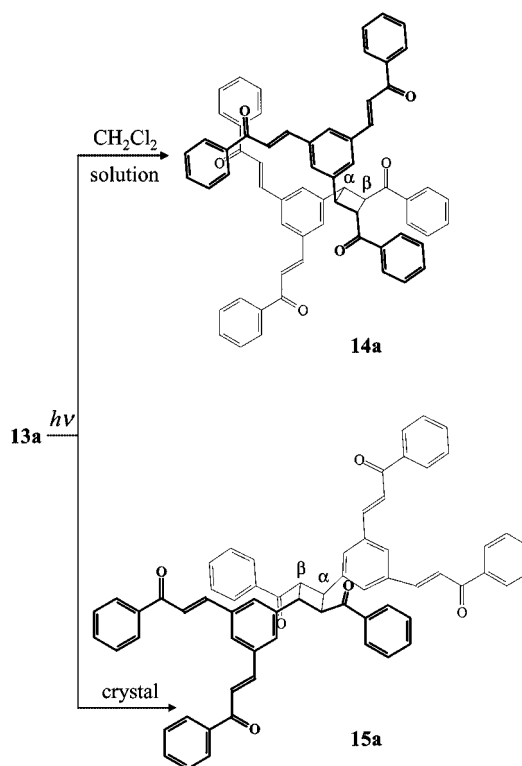
Threefold alkaline condensation of 1,3,5-benzenetricarbaldehyde (**11**) and the acetophenones **12a,b** leads to the compounds **13a,b** which are isomers of **7a,b**, but have the opposite direction of the enone substructures. (Scheme 6).^[16]



Scheme 6. Preparation of the (*E,E,E*)-1,3,5-tris(3-oxo-3-phenylpropenyl)benzenes **13a,b**.

The intramolecular mobility of the three arms in **13** is much lower than in **7** concerning the formation of excimers which are capable of cyclophane formation. Neither head-to-tail arrangements nor the distinction between *cisoid* or

transoid orientations of the enone units should play a role in this context. We expected a behavior, which is similar to 1,3,5-tristyrylbenzene,^[5,17–19] and should lead to a [2.2.2](1,3,5)cyclophane with C_{3h} or C_s symmetry.^[20] The irradiation of **13a** ($\lambda \geq 290 \text{ nm}$) in solution ($9.7 \times 10^{-2} \text{ M}$ in CH_2Cl_2 , $\lambda_{\text{max}} = 311 \text{ nm}$) yielded, as discussed for **7a**, a mixture of the four (*E*)/(*Z*) isomers, a dimer **14a** and a large amount of oligomers. Obviously, photopolymerization and photocrosslinking are much more effective for **13a** than for **7a**. Isolation of the dimer **14a** by preparative TLC and spectroscopic characterization led to the structure of a head-to-head adduct in which the two heads (as well as the two tails) have a *trans* arrangement (Scheme 7). Due to this stereochemistry, the distance between the remaining olefinic double bonds is too large to permit the formation of a second (and third) four-membered ring in an intramolecular process. However, intermolecular cycloadditions are feasible and yield oligomers as major products. The different behavior of **7** and **13** is due to the different intramolecular mobility of the monoadducts. The carbonyl groups act in the process **7** $\rightarrow$ **8** as a kind of “joints”, whereas in the monoadduct **14a** they are on the “wrong” side.



Scheme 7. *anti*-head-to-head photodimerization **13a** $\rightarrow$ **14a** in solution and *syn*-head-to-tail photodimerization **13a** $\rightarrow$ **15a** in the crystalline state.

Before we tried the photolysis of **13a** in the crystalline state, we performed a crystal structure analysis. Figure 2 shows the unit cell and the arrangement of neighboring molecules **13a** in the crystal. The molecules have nearly C_s symmetry and are located in parallel planes. However, the olefinic double bonds are in a distance which is much larger than $4.2 \text{ \AA}$. According to Schmidt's rule,^[21] a topochem-

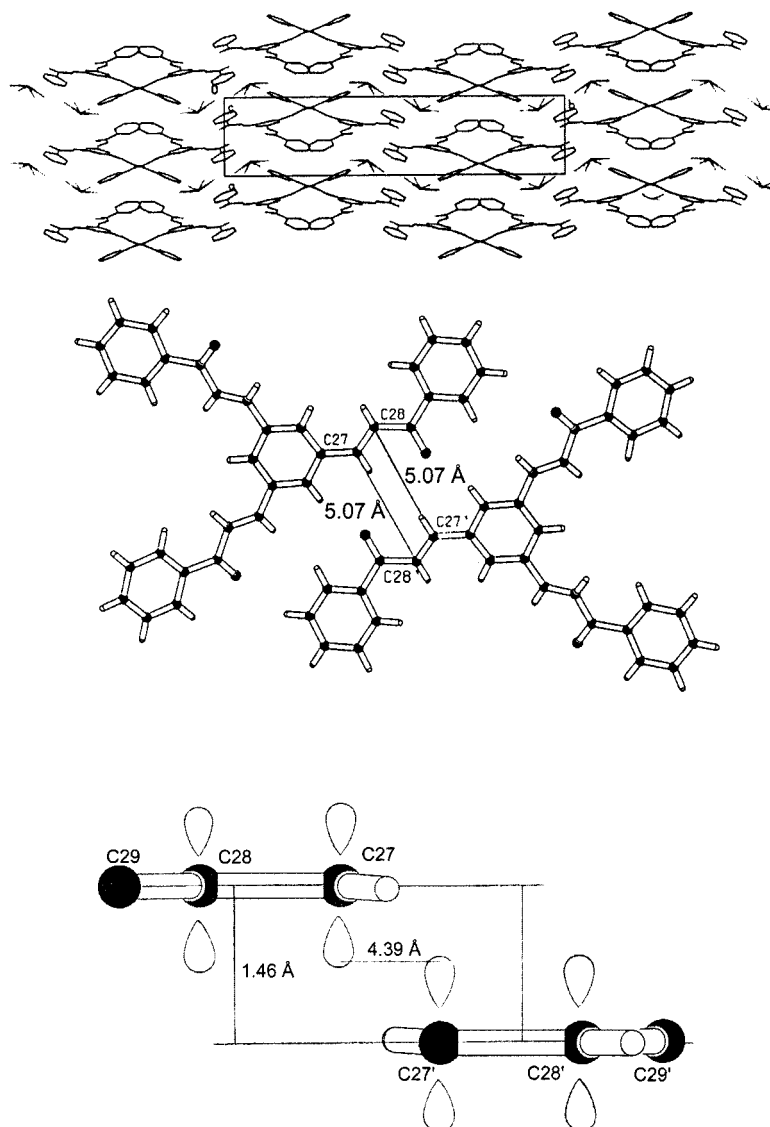


Figure 2. Top: Unit cell of **13a** (inclusion of solvent molecules CHCl_3). Center: Platon plot of neighboring molecules (all bond lengths and bond angles correspond to normal values). Bottom: Olefinic part in a view which is perpendicular to the view of the Platon plot.

ically controlled $[2\pi+2\pi]$ cycloaddition should be impossible. However, the experiment told us that the process is highly effective. The *syn*-head-to-tail adduct **15a** was obtained (Scheme 7) in a yield of 57%. We explain this result by the fact, that the parallel planes of the two reacting molecules have an ideal distance of 1.46 Å, which enables a sufficient interaction of the π -orbital of one component with the π^* -orbital of the other (Figure 2, bottom). As discussed for **14a**, dimer **15a** is not capable of further intramolecular $[2\pi+2\pi]$ photocycloaddition reactions.

Conclusions

Photocyclodimerizations of the parent chalcone were already studied in the 1920s by Stobbe,^[22,23] one of the early pioneers in photochemistry. However, structures of the dimers, obtained in solution, in the crystalline state and in the melt,^[24] led to a very long and controversial discussion,

until X-ray studies revealed, that in solution and in the molten state *anti*-head-to-head cycloadditions take place, whereas in the crystalline state *syn*-head-to-tail processes occur.^[24,25]

In principle, the photochemical behavior of the benzene derivatives studied here, with chalcone chromophores in 1,3,5-positions, resembles the behavior of the parent system – in solution as well as in the crystalline state. A special aspect is given by the threefold consecutive $[2\pi+2\pi]$ cycloaddition of **7** which leads in *anti*-head-to-head processes to [4.4.4](1,3,5)cyclophanes **8**. The enone segments react thereby selectively in the *cisoid* conformation. A related photoreaction was used by Hasegawa et al.^[26,27] for the topochemically controlled formation of [4.4](1,4)cyclophanes. The presence of cinnamic acid or ester units in cyclophanes can be used to close further bridges between the decks.^[28]

The opposite orientation of the enone units in **13** does not yield [2.2.2](1,3,5)cyclophanes. After the first *anti*-head-

to-head cycloaddition **13** → **14**, the intramolecular mobility is too low and the distance between the remaining double bonds too large to permit further intramolecular $[2\pi+2\pi]$ photocycloadditions.

The crystalline states of **7a** and **13a** are capable of efficient single *syn*-head-to-tail cycloadditions – even when the distance between the olefinic double bonds in neighboring molecules exceeds with 5.07 Å by far the value of 4.2 Å proposed in Schmidt's rule. We explain this result by the fact, that the planes of the C=C double bonds are parallel and have a short distance of 1.46 Å, which permits a sufficient overlap of the π - and the π^* -orbitals.

Experimental Section

General Remarks: UV/Vis: Zeiss MCS 320/340, CH₂Cl₂ as solvent. ¹H and ¹³C NMR: Bruker AMX 400, CDCl₃/TMS as internal standard. MS: Finnigan MAT 95 (FD, accelerating voltage 5 kV), Micromass QTOF Ultima-3 (ESI, reference: CsI/NaI standard solution), DSC: Perkin–Elmer DSC7. Melting points: Stuart Scientific SMP/3; values uncorrected.

(E)-1-{3,5-Bis[(E)-3-phenylacryloyl]phenyl}-3-phenylpropenone [all-(E)-1,3,5-Tricinnamoylbenzene (7a**)]:** Preparation according to the literature,^[10,11] yield 1.8 g (70%), m.p. 179 °C. ¹H NMR (CDCl₃): δ = 7.45 (m, 9 H, *m*-H, *p*-H, phenyl), 7.65 (d, ³*J* = 15.6 Hz, 3 H, 2-H), 7.70 (m, 6 H, *o*-H, phenyl), 7.93 (d, ³*J* = 15.6 Hz, 3 H, 3-H), 8.84 (s, 3 H, aromat. H, central benzene ring) ppm. ¹³C NMR (CDCl₃): δ = 121.1 (C-2), 128.8, 129.1 (*o*-, *m*-CH, phenyl), 131.1, 131.8 (aromat. CH, *p*-C, phenyl and central benzene ring), 134.5 (*i*-C, phenyl), 139.1 (C_q, central benzene ring), 146.4 (C-3), 188.9 (C-1) ppm. FD MS: *m/z* (%) = 469 (100) [M + H⁺]. HR MS: calcd. for C₃₃H₃₄O₃ 468.1725; found 468.1708. UV/Vis (CH₂Cl₂): λ_{max} = 326 nm; ϵ_{max} = 69040 cm² mol⁻¹.

Condensation Reaction of 1,3,5-Triacetylbenzene (5**) with 3,4,5-Trimethoxybenzaldehyde (**6b**):** Ketone **5** (0.57 g, 2.8 mmol) and NaOH (128 mg, 3.2 mmol) were warmed in C₂H₅OH (40 mL)/H₂O (60 mL) to 40 °C before aldehyde **6b** (2.74 g, 14.0 mmol), dissolved in C₂H₅OH (20 mL), was slowly added. The colorless solution turned orange-red and a solid precipitated. After 5 h of stirring at 40 °C, CHCl₃ was added so that the precipitate was dissolved. The organic layer was washed with the same amount of H₂O and saturated aqueous NaCl solution, dried with MgSO₄, and the solvents were evaporated. Column chromatography (3 × 50 cm SiO₂; toluene/ethyl acetate, 9:1) yielded excess **6b**, 264 mg (25%) of monocondensation product, 306 mg (20%) of dicondensation product and 71 mg (3%) of tricondensation product **7b**.

(E)-1-(3,5-Diacetylphenyl)-3-(3,4,5-trimethoxyphenyl)propenone: Yellowish solid, m.p. 154 °C. ¹H NMR (CDCl₃): δ = 2.71 (s, 6 H, CH₃), 3.89 (s, 3 H, *p*-OCH₃), 3.91 (s, 6 H, *m*-OCH₃), 6.88 (s, 2 H, *o*-H, trimethoxyphenyl), 7.43/7.79 (AB, ³*J* = 15.6 Hz, olefin. H), 8.69 (“s”, 1 H, *p*-H, phenyl), 8.70 (“s”, 2 H, *o*-H, phenyl) ppm. ¹³C NMR (CDCl₃): δ = 26.9 (CH₃), 56.4 (*m*-OCH₃), 61.0 (*p*-OCH₃), 106.2 (*o*-CH, trimethoxyphenyl), 120.0 (C-2), 129.8 (*i*-C, trimethoxyphenyl), 131.4 (*p*-CH, phenyl), 131.9 (*o*-CH, phenyl), 141.1 (*p*-C_qO, trimethoxyphenyl), 146.8 (C-3), 153.6 (*m*-C_qO, trimethoxyphenyl), 188.7 (C-1), 196.8 (CO, acetyl) ppm. FD MS: *m/z* (%) = 383 (100) [M + H⁺]. C₂₂H₂₂O₆ (382.1): calcd. C 69.10, H 5.80; found C 69.45, H 5.86.

(E)-1-{3-Acetyl-5-[(E)-3-(3,4,5-trimethoxyphenyl)acryloyl]phenyl}-3-(3,4,5-trimethoxyphenyl)propenone: Yellowish solid, m.p. 134 °C.

¹H NMR (CDCl₃): δ = 2.74 (s, 3 H, CH₃), 3.90 (s, 6 H, *p*-OCH₃), 3.93 (s, 12 H, *m*-OCH₃), 6.89 (s, 4 H, *o*-H, trimethoxyphenyl), 7.48/7.81 (AB, ³*J* = 15.6 Hz, 4 H, olefin. H), 8.66 (“s”, 2 H, *o*-H, phenyl), 8.76 (“s”, 1 H, *p*-H, phenyl) ppm. ¹³C NMR (CDCl₃): δ = 27.0 (CH₃), 56.4 (*m*-OCH₃), 61.1 (*p*-OCH₃), 106.2 (*o*-CH, trimethoxyphenyl), 120.0 (C-2), 129.8 (*i*-C, trimethoxyphenyl), 131.6, 132.1 (CH, phenyl), 137.8, 139.1 (C_q, phenyl), 141.1 (*p*-C_qO), 146.8 (C-3), 153.6 (*m*-C_qO), 188.9 (C-1), 197.1 (CO, acetyl) ppm. FD MS: *m/z* (%) = 561 (100) [M + H⁺]. C₃₂H₃₂O₉ (560.2): calcd. C 68.56, H 5.75; found C 68.45, H 5.89.

(E)-1-{3,5-Bis[(E)-3-(3,4,5-trimethoxyphenyl)acryloyl]phenyl}-3-(3,4,5-trimethoxyphenyl)propenone (7b**):** Yellowish solid, m.p. 208 °C. ¹H NMR (CDCl₃): δ = 3.91 (s, 9 H, *p*-OCH₃), 3.94 (s, 18 H, *m*-OCH₃), 6.91 (s, 6 H, *o*-H, trimethoxyphenyl), 7.52 (d, ³*J* = 15.4 Hz, 3 H, olefin. H), 7.84 (d, ³*J* = 15.4 Hz, 3 H, olefin. H), 8.83 (s, 3 H, aromat. H, central benzene ring) ppm. ¹³C NMR (CDCl₃): δ = 56.4 (*m*-OCH₃), 61.0 (*p*-OCH₃), 106.2 (*o*-CH, trimethoxyphenyl), 120.2, 146.8 (olefin. CH), 129.8 (*i*-C, trimethoxyphenyl), 131.7 (aromat. CH, central benzene ring), 139.2 (C_q, central benzene ring), 141.1 (*p*-C_qO), 153.6 (*m*-C_qO), 189.0 (CO) ppm. FD MS: *m/z* (%) = 739 (100) [M + H⁺]. HR MS: calcd. for [C₄₂H₄₂O₁₂ + Na⁺] 761.2574; found 761.2468.

(E)-1-{3,5-Bis[(E)-3-(3,4,5-trihexyloxyphenyl)acryloyl]phenyl}-3-(3,4,5-trihexyloxyphenyl)propenone (7c**):** Preparation analogous to **7a**. After 1 d of stirring in the dark, the solution was neutralized with HCl and extracted with CH₂Cl₂. The organic layer was washed with saturated aqueous NaCl solution and H₂O, dried with MgSO₄, and the solvents were evaporated. Column chromatography (3 × 40 cm SiO₂; gradient toluene/ethyl acetate, 10:0 to 10:1) yielded 268 mg (18%) of a yellowish solid which showed a single phase transition in the DSC at 169.0 °C (onset temperature, heating curve with a rate of 10 °C min⁻¹). ¹H NMR (CDCl₃): δ = 0.90 (m, 27 H, CH₃), 1.33–1.40 (m, 54 H, CH₂), 1.77 (m, 18 H, CH₂), 4.00 (m, 18 H, OCH₂), 6.90 (s, 6 H, *o*-H, trihexyloxyphenyl), 7.49 (d, ³*J* = 15.6 Hz, 3 H, 2-H), 7.88 (d, ³*J* = 15.6 Hz, 3 H, 3-H), 8.77 (s, 3 H, aromat. H, central benzene ring) ppm. ¹³C NMR (CDCl₃): δ = 13.0, 13.0 (CH₃), 21.8, 25.0, 28.6, 29.6, 31.0 (CH₂, partly superimposed), 68.5 (*m*-OCH₂), 72.8 (*p*-OCH₂), 106.5 (*o*-CH, trihexyloxyphenyl), 119.6, 145.8 (olefin. CH), 128.8 (*i*-C, trihexyloxyphenyl), 130.6 (aromat. CH, central benzene ring), 138.7 (C_q, central benzene ring), 140.4 (*p*-C_qO), 152.7 (*m*-C_qO), 188.4 (CO) ppm. FD MS: *m/z* (%) = 1369 (100) [M⁺]. HR MS (ESI): calcd. for [C₈₇H₁₃₂O₁₂ + Na⁺] 1391.9617; found 1391.9585. UV/Vis (CH₂Cl₂): λ_{max} = 365 nm; ϵ_{max} = 64905 cm² mol⁻¹.

(E)-1-{3,5-Bis[(E)-3-(3,4,5-tridodecyloxyphenyl)acryloyl]phenyl}-3-(3,4,5-tridodecyloxyphenyl)propenone (7d**):** Preparation and workup as described for **7c**. Yield 354 mg (30%) of a yellowish waxy solid, which showed in the DSC a transition to the isotropic phase at 123.7 °C (onset temperature, 2nd heating curve, rate: 10 °C min⁻¹). The 2nd heating curve contains two further overlapping peaks with maxima at 20 and 27 °C which might point to an LC phase. ¹H NMR (CDCl₃): δ = 0.85 (m, 27 H, CH₃), 1.24–1.46 (m, 162 H, CH₂), 1.78 (m, 18 H, CH₂), 4.00 (m, 18 H, OCH₂), 6.87 (s, 6 H, *o*-H, tridodecyloxyphenyl), 7.46 (d, ³*J* = 15.2 Hz, 3 H, 2-H), 7.80 (d, ³*J* = 15.2 Hz, 3 H, 3-H), 8.80 (s, 3 H, aromat. H, central benzene ring) ppm. ¹³C NMR (CDCl₃): δ = 14.1, 14.1 (CH₃), 22.7, 26.1, 29.7, 29.7, 32.0 (CH₂, partly superimposed), 69.4 (*m*-OCH₂), 73.7 (*p*-OCH₂), 107.6 (*o*-CH, tridodecyloxyphenyl), 119.9, 147.2 (olefin. CH), 126.9 (*i*-C, tridodecyloxyphenyl), 129.4 (aromat. CH, phenyl), 139.4 (C_q, central benzene ring), 141.5 (*p*-C_qO), 153.5 (*m*-C_qO), 189.3 (CO) ppm. FD MS: *m/z* (%) = 2127 (100) [M⁺]. HR MS (ESI): calcd. for [C₁₄₁H₂₄₀O₁₂ + Na⁺] 2148.8068; found 2148.7986.

Irradiation of 7a in Solution: A solution of **7a** (50 mg, 0.11 mmol) in CH₂Cl₂ (or CD₂Cl₂) (0.75 mL) was irradiated with a high-pressure QSL lamp equipped with a Pyrex filter for 1.5 h. Addition of petroleum ether (b.p. 40–60 °C) (5 mL) yielded 29 mg (58 %) of pure cyclophane **8a** (structure **8ab**) which melted at 248 °C (decomp.). ¹H NMR (CDCl₃): δ = 3.90/4.47 (AA'BB', 12 H, cyclobutane rings), 7.20–7.40 (AA'BB'C, 30 H, phenyl groups), 7.81 (s, 6 H, aromat. H, central benzene rings) ppm. ¹³C NMR (CDCl₃): δ = 41.7 (β-C, cyclobutane), 52.9 (α-C, cyclobutane), 127.0 (o-CH, phenyl), 128.9 (m-CH, phenyl), 127.4 (p-CH, phenyl), 131.4 (CH, central benzene ring), 140.4, 140.6 (i-C, phenyl and C_q, central benzene ring), 197.8 (CO).^[29] The same irradiation of a less concentrated solution (2.9 × 10⁻² M, CD₂Cl₂) was used for the determination of the photochemically formed isomers of **7a**/(*E,E,E*)/(*E,E,Z*)/(*E,Z,Z*)/(*Z,Z,Z*) = 2:4:8:5. The integration of the ¹H NMR signals of the protons on the central benzene ring (the A₃ and A₂M spin patterns between δ = 8.5 and 8.9 ppm) served for the quantitative determination.

Irradiation of a 2:1 Mixture of 7a/7b: Irradiation and workup as described for **7a**. The product mixture had a ratio of **9/8b/8a** = 77:19:≤4 according to the ¹H NMR spectrum. Since **9** is by far the major product, the mixture could be directly used for the NOE measurement.

Irradiation of 7a in the Crystalline State: **7a** (260 mg, 0.56 mmol) was crystallized from the melt on a 10 × 10 cm glass plate and irradiated with a Hanovia 450 W lamp equipped with a Pyrex filter. At the end of the reaction (TLC control: SiO₂; toluene/ethyl acetate, 50:1), the material was flushed in CHCl₃. After evaporation of the solvent, portions of 30 mg of the residue were purified by preparative TLC (20 × 20 cm SiO₂; toluene/ethyl acetate, 50:1). Each portion yielded 20 mg (66%) of a colorless solid **10a** which melted at 190 °C. ¹H NMR (CDCl₃): δ = 4.94/5.16 (AA'BB', 4 H, cyclobutane), 7.30/7.12/7.01 (AA'BB'C, 10 H, phenyl groups on cyclobutane ring), 7.68/7.45/7.45 (AA'BB'C, 20 H, phenyl groups on olefinic double bonds), 7.52/7.87 (AB, ³J = 15.8 Hz, 4 H, olefin. H), 8.46/8.67 (A₂B, ⁴J = 1.5 Hz, central benzene rings) ppm. ¹³C NMR (CDCl₃): δ = 42.3 (β-C, cyclobutane), 51.2 (α-C, cyclobutane), 120.9, 146.3 (olefin. CH), 127.4 (p-CH, phenyl groups on cyclobutane), 128.2 (o-CH, phenyl groups on cyclobutane), 128.5 (m-CH, phenyl groups on cyclobutane), 128.7 (o-CH, phenyl groups on olefinic double bonds), 129.0 (m-CH, phenyl groups on olefinic double bonds), 131.1 (p-CH, phenyl groups on olefinic double bonds), 131.4/131.7 (CH, central benzene ring), 134.4 (i-C, phenyl groups on olefinic double bonds), 137.4 (i-C, phenyl groups on cyclobutane), 138.4, 138.6 (C_q, central benzene ring), 188.6 (CO, cinnamoyl), 197.7 (CO) ppm.^[29] FD MS: *m/z* (%) = 936 (100) [M⁺]. HR MS (ESI): calcd. for [C₆₆H₄₈O₆ + Na⁺] 959.3349; found 959.3353.

(*E,E,E*)-1,3,5-Tris(3-oxo-3-phenylpropen-1-yl)benzene (13a): A mixture of trialdehyde **11** (162 mg, 1.0 mmol), acetophenone **12a** (420 mg, 3.5 mmol) and KOH (28 mg, 0.5 mmol) in dry methanol (11 mL) was stirred in the presence of 4-Å molecular sieves at ambient temperature. A colorless precipitate was formed and the reaction was stopped after 24 h. The solid was recrystallized from diethyl ether to which ethanol was added until the boiling solution became turbid. Yield 282 mg (60%), m.p. 194 °C (ref.^[12] 187 °C). ¹H NMR (CDCl₃): δ = 8.04/7.51/7.58, m, 3 H (AA'BB', 15 H, aromat. H, phenyl), 7.62/7.82 (AB, ³J = 15.8 Hz, 6 H, olefin. H) ppm. ¹³C NMR (CDCl₃): δ = 123.8 (β-CH), 128.6, 128.7 (o-CH, m-CH, phenyl), 129.4 (HC-2), 133.1 (p-CH, phenyl), 136.5, 137.8 (aromat. C_q), 142.9 (α-CH), 190.0 (CO) ppm.^[29] FD MS: *m/z* (%) = 469 (100) [M + H⁺]. HR MS (ESI): calcd. for [C₃₃H₂₄O₃ + Na⁺]

491.1623; found 491.1642. UV/Vis (CH₂Cl₂): λ_{max} = 311 nm; ε_{max} = 74160 cm² mol⁻¹.

(*E,E,E*)-1,3,5-Tris[3-oxo-3-(3,4,5-trimethoxyphenyl)propen-1-yl]benzene (13b): Preparation as described for **13a** yielded 280 mg (38%) of product which still contained some impurities. Column chromatography (3 × 30 cm Al₂O₃, CHCl₃) gave 110 mg (15%) of highly pure yellowish solid, which melted at 98 °C. ¹H NMR (CDCl₃): δ = 3.91 (s, 9 H, OCH₃), 3.92 (s, 18 H, OCH₃), 7.26 (s, 6 H, aromat. H, outer benzene rings), 7.56/7.82 (AB, ³J = 15.8 Hz, 6 H, olefin. H), 7.86 (s, 3 H, aromat. H, central benzene ring) ppm. ¹³C NMR (CDCl₃): δ = 56.5 (6 OCH₃), 61.0 (3 OCH₃), 106.2 (aromat. CH, outer benzene rings), 123.4 (β-CH), 129.4 (HC-2, phenyl), 132.9 (C_q, outer benzene rings), 136.5 (C-1), 142.7 (α-CH), 142.9, 153.2 (C_qO), 188.6 (CO) ppm.^[29] FD MS: *m/z* (%) = 739 (100) [M + H⁺]. HR MS (ESI): calcd. for [C₄₂H₄₂O₁₂ + Na⁺] 761.2574; found 761.2563.

Irradiation of 13a in Solution: A solution of **13a** (150 mg, 0.32 mmol) in CH₂Cl₂ (3.3 mL) (*c* = 9.7 × 10⁻² M) was irradiated with a QSL lamp equipped with a Pyrex filter for 3 h. The obtained oligomer mixture was purified by column chromatography (2 × 30 cm SiO₂; CH₂Cl₂/H₃CCOOC₂H₅, 20:1). The first fractions, which contained **14a** and low oligomers, were then used for preparative TLC [20 × 20 cm SiO₂; petroleum ether (b.p. 40–60 °C)/diethyl ether, 1:3]. Pure dimer **14a** was obtained in a yield of 7 mg per TLC plate (yield 6%). It is an almost colorless solid which starts to decompose at 200 °C. ¹H NMR (CDCl₃): δ = 4.14/4.65 (AA'BB', 4 H, cyclobutane ring), 7.86/7.34/7.59 (AA'BB'C, 10 H, benzoyl groups on cyclobutane), 7.98/7.50/7.56 (AA'BB'C, 20 H, aromat. H, benzoyl groups on olefinic double bonds), 7.59/7.77 (AB, ³J = 15.8 Hz, 8 H, olefin. H), 7.61 (m, 4 H, aromat. H, central benzene ring), 7.79 (m, 2 H, aromat. H, central benzene ring) ppm. ¹³C NMR (CDCl₃): δ = 46.8, 47.7 (CH, cyclobutane ring), 123.5, 143.2 (olefin. CH), 127.3, 129.8 (aromat. CH, central benzene ring), 128.6, 128.7, 133.0 (aromat. CH, benzoyl group on olefinic double bond), 128.8, 128.9, 134.0 (aromat. CH, benzoyl group on cyclobutane ring), 135.2, 136.4 (aromat. C_q, central benzene ring), 137.8, 142.8 (aromat. C_q, benzoyl groups), 190.1 (CO, enone), 198.4 (CO) ppm. FD MS: *m/z* (%) = 938 (100) [M⁺]. HR MS (ESI): calcd. for [C₆₆H₄₈O₆ + Na⁺] 959.3349; found 959.3364.

Irradiation of 13a in the Crystalline State: **13a** (66 mg, 0.14 mmol) was irradiated as described for **7a**. The obtained dimer **15a** (38 mg, 57%) is an almost colorless solid which starts to decompose above 120 °C. ¹H NMR (CDCl₃): δ = 4.95/5.65 (AA'BB', 4 H, cyclobutane ring), 7.77/7.32/7.40 (AA'BB'C, 10 H, aromat. H, benzoyl group on cyclobutane ring), 7.42/7.66 (AB, ³J = 15.8 Hz, 4 H, olefin. H), 8.01/7.53/7.61 (AA'BB'C, 20 H, aromat. H, benzoyl group on olefinic double bond), 7.55 (m, 6 H, aromat. H, central benzene ring) ppm. ¹³C NMR (CDCl₃): δ = 42.0 (β-CH, cyclobutane), 50.0 (α-CH, cyclobutane), 123.2, 143.4 (olefin. CH), 126.9, 129.6 (aromat. CH, central benzene ring), 128.2, 128.6, 133.5 (CH, benzoyl group on cyclobutane ring), 128.6, 128.7, 133.0 (CH, benzoyl group on olefinic double bond), 135.7, 136.3, 137.9, 140.3 (aromat. C_q), 190.2 (CO, enone), 198.2 (CO) ppm.^[27] FD MS: *m/z* (%) = 937 (84) [M + H⁺], 469 (100) [M + 2 H⁺]. HR MS (ESI): calcd. for [C₆₆H₄₈O₆ + Na⁺] 959.3349; found 959.3324.

Crystal Structure Analysis of 13a: The measurements were carried out with an Enraf–Nonius CAD-4-diffractometer with the software Collect V5 (Enraf–Nonius B.V., Delft, The Netherlands, 1989). The structure was solved with SIR 92^[30] and refined by full-matrix least-squares technique on *F*² with SHELXL-97.^[31] Details on the X-ray crystal structure analysis are listed in Table 2. CCDC-634439 contains 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.

Table 2. Details of the X-ray crystal structure analysis of (*E,E,E*)-1,3,5-tris(3-oxo-3-phenylpropenyl)benzene (**13a**).

Empirical formula	C ₃₃ H ₂₄ O ₃ ·CHCl ₃
Formula mass	587.9
Habit	yellow block
Crystal size [mm]	0.2 × 0.25 × 0.4
Space group	<i>P</i> 2 ₁ / <i>c</i> (monoclinic)
Cell constants:	
<i>a</i> [Å]	7.810(3)
<i>b</i> [Å]	34.241(3)
<i>c</i> [Å]	10.645(4)
β [°]	90.98(2)
<i>V</i> [Å ³]	2846(2)
<i>Z</i>	4
<i>D</i> _x [Mg m ⁻³]	1.372
Radiation	Cu-K α
μ [mm ⁻¹]	3.19
<i>F</i> (000)	1216
<i>T</i> [K]	193
$\theta_{\max}$ [°]	74
No. of reflections:	
measured	6202
independent	5771
observed [$ F /\sigma(F) > 4.0$]	4336
<i>R</i> _{σ}	0.0288
Parameters	379
<i>wR</i> (<i>F</i> ² , all reflections)	0.1617
<i>R</i> [<i>F</i> ² , >2 σ (<i>F</i> ²)]	0.0583
<i>S</i>	1.042
Max. $\Delta\rho$ [e Å ⁻³]	0.43
Min. $\Delta\rho$ [e Å ⁻³]	-0.57

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