Synthesis and Topochemistry of 2,5-Bisacrylate-Substituted 1,4-Benzoquinones☆

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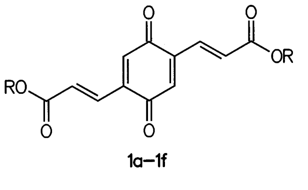
The 2,5-bisacrylate-substituted 1,4-benzoquinone bisketal **7a** was synthesized by electrochemical oxidation of the corresponding dimethoxybenzene **6**. The methyl ester **7a** was transesterified to the corresponding ethyl, *n*-propyl and isopropyl esters **7b**−**7d** by $Ti(OEt)_4$ catalysis and to the corresponding *n*-butyl and benzyl esters **7e**−**7f** by the Li alkoxides. The bisketals **7a**−**7f** were hydrolyzed to the corresponding 2,5-bisacrylate-substituted 1,4-benzoquinones **1a**−**1f**. The crystal structure of the ethyl ester **1b** was determined by X-ray diffraction, which revealed short intermolecular contacts of 3.463 and 4.051 Å between vinyl groups and quinone double bonds, respectively, related by twofold symmetry. Because of the shorter distance and the smaller shift in projection (vinyl: 1.002; quinone: 2.107 Å), only the vinyl group is photoactive in the crystal. In the solid state, topochemically controlled [2+2] photocycloadditions take place at the vinylic groups of the bisvinyl quinones **1a**−**1f**, to afford dimers and oligomers (n_{max} = 7), under topochemical control. The cyclobutane units generated from **1b** and from **1c**−**1f** have twofold and centric symmetry, respectively, as determined by ^{1}H-NMR spectroscopy and simulation thereof. The twofold symmetry in the cycloaddition products of **1b** is in agreement with the crystal structure of the monomers.

Irradiation of methyl-substituted *p*-benzoquinones in the crystalline state (topochemistry) results in stereospecific [2+2] cycloaddition reactions to form cyclobutanes, tetra-asteranones and oxetanes[1]. Phenyl and heteroaryl systems substituted in their *para* positions by two vinyl groups may be photo-oligomerized and -polymerized with high stereospecificity in the crystalline state by repeating [2+2] cycloadditions[2]. Even absolute asymmetric syntheses can be performed by topochemical reactions[3]. We have combined both systems of quinone and vinylbenzene compounds to quinone derivatives substituted by two styrene groups and performed topochemical reactions[4]. In this paper we describe the synthesis, the structural determination and the topochemical behaviour of (*E*,*E*)-2,5-bis(2-alkoxycarbonylethenyl)-1,4-benzoquinones **1**[5].

Scheme 1. Formula scheme of compounds **1a**−**1f**



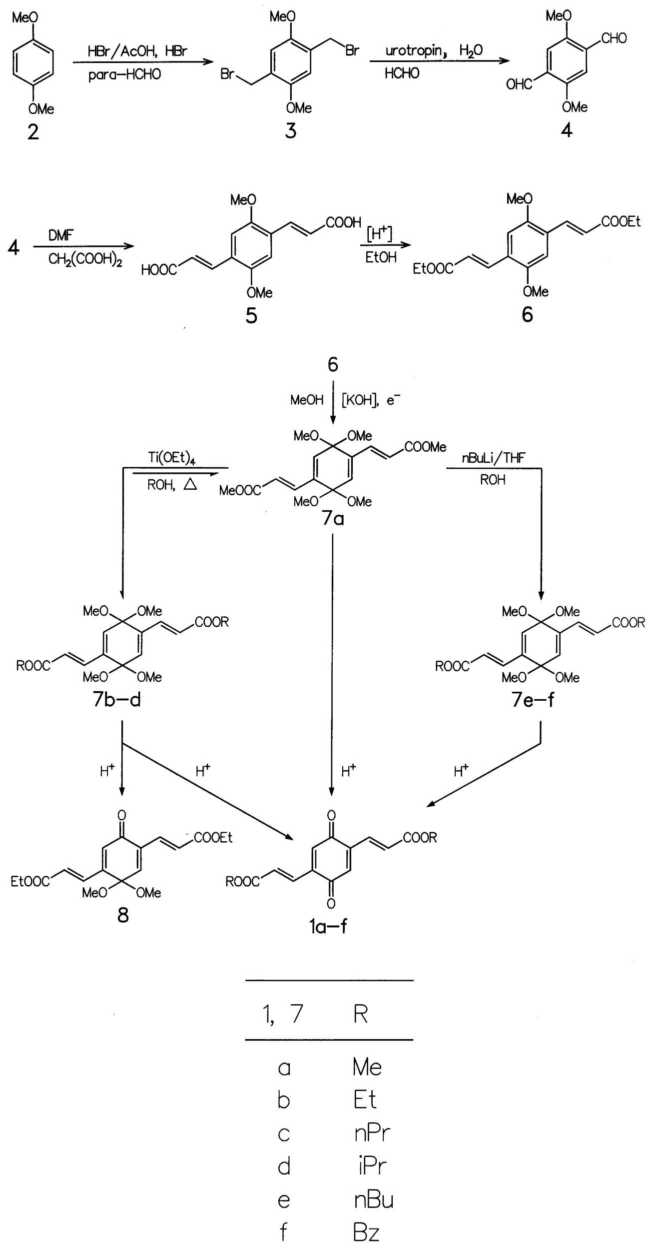
1a−1f

1	R
a	Me
b	Et
c	nPr
d	iPr
e	nBu
f	Bz

Syntheses of (*E*,*E*)-2,5-Bis(2-alkoxycarbonylethenyl)-1,4-benzoquinones 1

1,4-Dimethoxybenzene (**2**) was bisbromomethylated in glacial acetic acid solution with paraformaldehyde and hydrogen bromide to compound **3**. By this method, the Blanc reaction, where chloromethylation leads to the formation of carcinogenic byproducts, could be avoided[6]. The terephthalaldehyde **4** could be obtained by a Sommelet reaction. By a Knoevenagel-Doebner condensation with malonic acid in DMF solution, the *p*-phenylenebisacrylic acid **5** was synthesized in a 96% yield. The diacid **5** was transformed to the diethyl diester **6** in a 94% yield. We chose the ethyl ester group because compound **6** is more soluble in methanol than the corresponding methyl ester derivative. Since an ether cleavage of vinyl-substituted 1,4-dimethoxybenzenes is not possible[4b], the aromatic dimethoxybenzene derivative **6** was electrochemically oxidized to the quinone bisketal **7a** (59% yield) in methanolic solution with KOH as the conducting agent, at room temperature. Simultaneously, a transesterification to the methyl ester takes place. The ethyl, *n*-propyl and isopropyl esters **7b**−**7d** were derived from the methyl ester **7a** by refluxing in a solution of the corresponding alcohol with tetraethoxytitanium as catalyst. The *n*-butyl and benzyl esters **7e** and **7f**, respectively, could be obtained by the reaction of the methyl ester **7a** with the corresponding lithium alkoxides in THF solution at 0°C. In acetone solution, with catalytic amounts of 2 N sulfuric acid, the ketals **7a**−**7f** were hydrolyzed to the corresponding quinones **1a**−**1f** at room temperature. The hydrolysis of the ketal groups is much faster than the hydrolysis of the ester groups. The quinones **1a**−**1f** crystallize from the acetone solutions because of their limited solubility. The isolated yields were 70−99% for **1a**−**1e**, and 48% for **1f**. The compounds were characterized by ^{1}H- and ^{13}C-NMR, IR, and UV/Vis spectroscopy and mass spectrometry. Compounds **5** and **6** show strong fluorescence emission. In the course of the acidic hydrolysis of the ketal **7b** in DMF/H_2O solution, the semiketal **8** was formed.

Scheme 2. Synthesis of the *(E,E)*-2,5-bis(2-alkoxycarbonylethenyl)-1,4-benzoquinones **1**

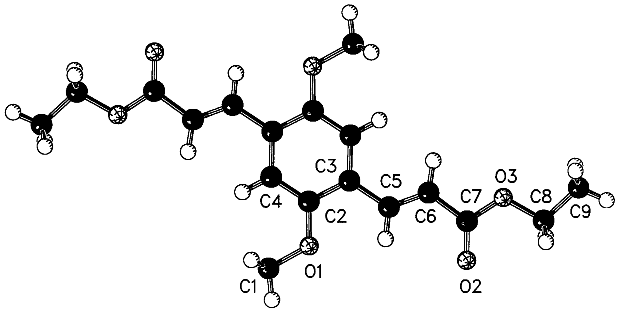


1, 7	R
a	Me
b	Et
c	nPr
d	iPr
e	nBu
f	Bz

Crystal and Molecular Structures of Compounds 6, 7a and 8

The vinyl-substituted 1,4-dimethoxybenzene **6** crystallizes in the monoclinic space group *C2/c* with $Z = 4$. Therefore the molecules lie on crystallographic centres of symmetry. They have a planar arrangement (Figure 1). The molecular parameters of **6** are in agreement with the corresponding values of comparable compounds[4b][7]. The shortest cell dimension is $b = 4.1065(7)$ Å. Therefore the vinylic double bond has this short contact to the corresponding bond of a neighbouring molecule. Despite this topochemically favourable distance, the crystals are photostable, since the parallel double bonds are shifted by 2.093 Å perpendicular to the bond axis, causing an unfavourable overlap of their π systems. The 61.0° angle between the molecular plane and the stacking axis is also unfavourable for topochemical cycloadditions between these kinds of molecules[4a].

Figure 1. Molecular structure of compound **6** with labelling[14]; C2−C3 1.404(3), C2−C4 1.381(3), C3−C4′ 1.393(3), C3−C5 1.469(3), C5−C6 1.300(3), C6−C7 1.479(3) Å

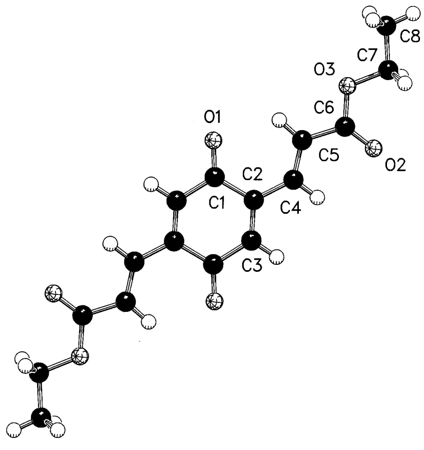


The quinone bisketal **7a** also crystallizes with a molecular centre of symmetry C_i ($P\bar{1}$; $Z = 1$).[13] The methoxy groups have a *gauche/anti* orientation.[8] The methoxy groups of the semiketal **8** have an *anti/anti* orientation in the crystal.[13]

Crystal and Molecular Structure of the Quinone 1b

Crystals suitable for X-ray structure analysis of the quinones **1** could only be obtained for derivative **1b**. The C_{2h} molecular symmetry coincides completely with crystallographic symmetry elements, (*Cmca*; $Z = 4$). Such highly symmetrical molecular arrangements are rarely found in crystals. The vinylic double bond of quinone **1b** has an *s-trans* conformation in contrast to other quinones substituted by two styrene groups[4b] (Figure 2).

Figure 2. Molecular structure of compound **1b** with labelling; C1−C2 1.502(12), C2−C3 1.332(11), C1−C3′ 1.470(12), C2−C4 1.461(12), C4−C5 1.337(10), C5−C6 1.475(12) Å



The molecules in the crystal are stacked in the crystallographic mirror planes perpendicular to the *a* axis in an ABAB... sequence and are related by a twofold rotation axis

(Figure 3). Two quinone double bonds C2−C3 of neighbouring molecules (contact 1, *A*: $-1/2 + x, y, 11/2 - z$) and two olefinic double bonds C4−C5 (contact 2) have short distances below the topochemical limit of 4.2 Å (Table 1; Figure 3). The quinone double bonds have a relatively small crossing angle φ but long intermolecular distances and a very large shift parameter *d*. On the other hand, the vinylic double bonds have short contacts and a small shift parameter *d* but a relatively large crossing angle φ. Therefore the second contact seems to be more suitable for a photochemical [2+2] cycloaddition reaction.

Figure 3. Packing arrangement of compound **1b**

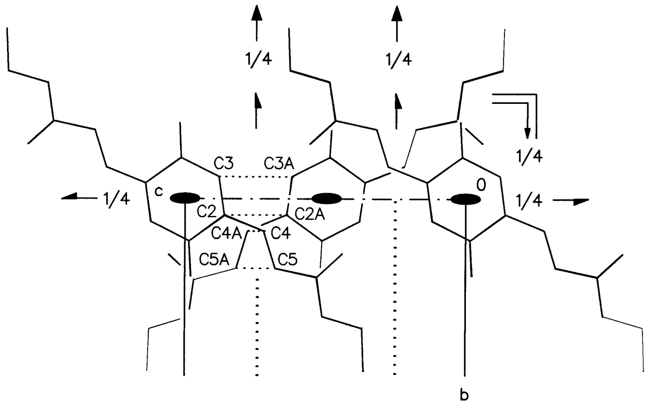
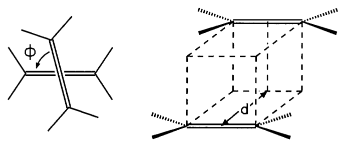


Table 1. Intermolecular contacts of compound **1b** in the crystal

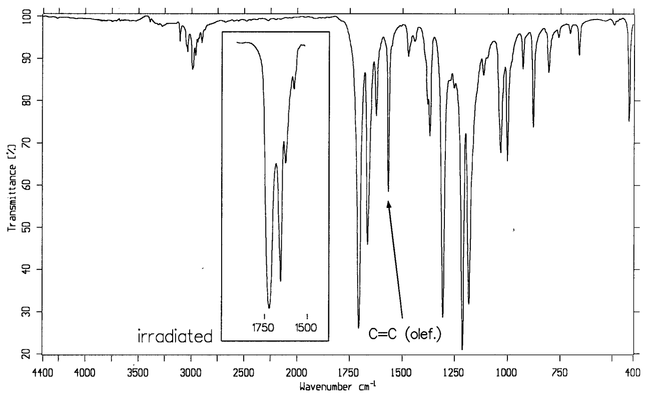


contact no.	contact	distance [Å]	double bonds φ [°]	*d* [Å]
1	C3···C3A	4.157(8)	16.0	2.107
	C2···C2A	3.944(7)		
2	C5···C5A	3.570(4)	34.0	1.002
	C4···C4A	3.355(2)		

Photochemical Reactions of the Quinones 1a−1f in the Crystalline State

We irradiated an aqueous suspension of powdered crystals of the quinones **1a**−**1e** with unfiltered UV light from a high-pressure mercury lamp (150 W), in a dipping-lamp apparatus for 12 h. The suspension was stirred vigorously, and the temperature was kept constant at 20°C by cooling. We separated the product, which became dark during the irradiation. Only a part of this material was soluble in $CHCl_3$. The IR and ^1H-NMR spectra were too complex to be interpreted, probably because of decomposition products. We therefore chose more moderate irradiation conditions, with suitable filters. With a high-pressure mercury lamp (1200 W), we irradiated 50−100 mg of powdered crystals of **1a**−**1f**, distributed on an aluminium foil for 4 h at 20°C with filter A (absorption edge 405 nm) and then with filter B (absorption edge 520 nm). Before and after irradiation, IR spectra (KBr) were recorded. The bands of the IR spectra of the irradiation products were broadened. The most significant change before and after irradiation is observed at the C=C (vinyl) and C=C (quinone) signals. From the ratio between both intensities, a definite decrease of the vinyl intensity is observed for all quinones **1a**−**1f** (Table 11). For example, Figure 4 illustrates the changes of the IR spectrum of **1b**, produced by irradiation with filter B. In the IR spectra of the quinones **1a**−**1f** irradiated with filters A and B, no considerable differences can be detected. The IR data show that the vinylic double bond is mainly involved in these photoreactions.

Figure 4. IR spectra of the quinone **1b** before and after irradiation using filter B

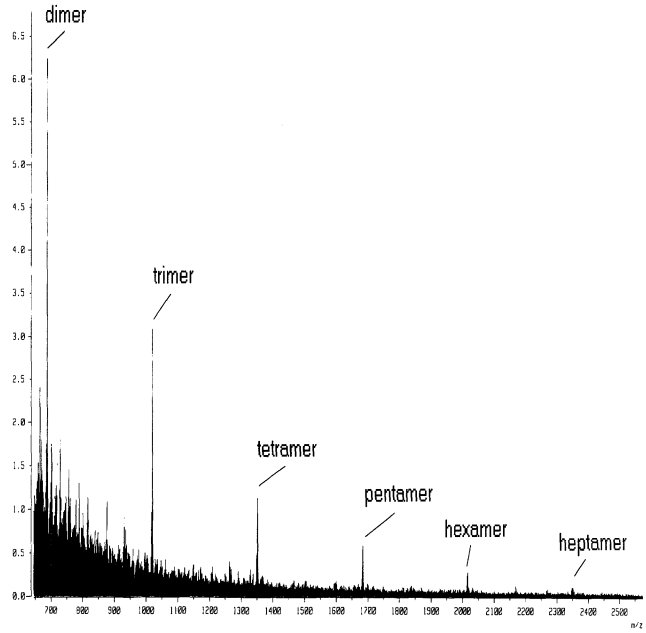


The FAB mass-spectra of the quinones **1a**−**1f** before the irradiation, and of their products after irradiation with filters A and B, were recorded. The relative intensities of the oligomers were calibrated to the intensities of the monomers, or in case of their absence, to the intensities of the dimers (Table 12). For the irradiation products of all samples, the formation of oligomers (up to $n = 7$) could be detected. It must also be noted that the FAB mass spectra of the quinones **1** before irradiation, show a small amount of oligomer peaks up to $n = 3$ because of cluster aggregation in the matrix (Table 12). Analysing the mass spectra of the oligomers affords a substraction of these components. The results of the irradiation with filters A and B are not significantly different.

The dimethyl ester **1a** is weakly photoreactive. Oligomers only up to $n = 3$ are generated. The relative amount of oligomers in the case of **1b**−**1f** is substantially larger (Table 12). In the mass spectrum of the irradiated quinone **1c**, even heptamers appear (Figure 5). After irradiation of the quinones **1c**−**1e**, no monomers remain. In the mass spectra, peaks of quinones and hydroquinones appear simultaneously. This is an indication of quinone subgroups in the oligomers.

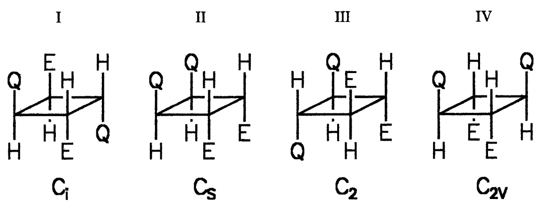
For NMR investigations, the irradiation products of **1b**−**1f** with filters A and B were dissolved completely in $CDCl_3$. The corresponding methyl esters of **1a** could not be dissolved in $CDCl_3$. In hot DMSO and DMF, decomposition takes place.

Figure 5. FAB-MS spectra of the quinone **1c** after irradiation using filter A



In the ^{1}H-NMR spectra of the irradiated **1b**−**1f**, new multiplets corresponding to four hydrogen atoms bonded to a four-membered ring appear at $\delta = 3.5-4.4$. These correspond to a cyclobutane ring generated by cycloaddition of vinyl groups. Singlets of cyclobutane protons produced by cycloaddition of quinoid double bonds could not be detected. There are no substantial differences in the spectra of the irradiation products with filters A and B. The coupling system of these protons is of the AA′BB′ type. Therefore the C_{2v}-symmetric substitution pattern IV (Figure 6) which requires an A_2B_2 coupling system can be disregarded.

Figure 6. All possible configurations of cyclobutane ring systems generated by irradiation of *trans* double bonds in the solid state, *trans*/*cis* isomerization excluded



To distinguish between the remaining three possibilities I−III (Figure 6) causing an AA′BB′ spin system, we simulated[9] these three types. The multiplet of the cyclobutane protons recorded for the irradiation product of **1b** fits very well with the C_2-symmetric simulation III (Figure 7) with a *trans* coupling of $^{3}J = 10$ Hz. The dimerization at the vinyl groups and the C_2 symmetry of the cyclobutanes are in agreement with the packing arrangement of the monomers **1b** in the crystal. In addition to the signals of the monomers, new signals for vinyl protons ($H_{A'}$ and $H_{B'}$) of dimers and oligomers are found further upfield (Table 2; Scheme 3). The quinoid protons H_C are no longer chemically equivalent ($H_{C'}$ and $H_{C''}$; Table 2) in dimers. For the oligomers, an additional signal (for $H_{C'''}$) appears. The signals for the protons of the ester groups are doubled (Figure 8, Scheme 3).

Figure 7. ^{1}H-NMR signals of the cyclobutane protons after irradiation of quinone **1b** using filter B (top) and simulated ^{1}H-NMR spectra of a cyclobutane ring with C_2 symmetry

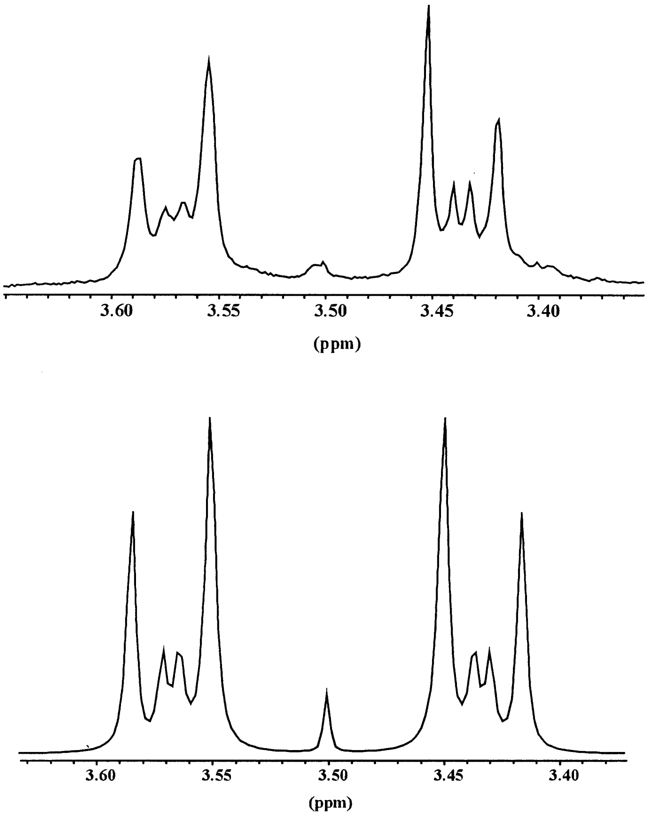


Table 2. ^{1}H-NMR data of the quinone **1b** after irradiation using filter B

proton	peak (δ)
H_A	7.483
$H_{A'}$	7.480
H_B	6.840
$H_{B'}$	6.817
H_C	6.900
$H_{C'}$	6.819
$H_{C''}$	6.760
$H_{C'''}$	6.677

The C_i simulation I (Figure 6, Figure 9) with a *trans* coupling of $^{3}J = 3.5$ Hz and a *cis* coupling of 4.8 Hz also fits very well with the multiplets of the cyclobutane protons recorded for the irradiation products of the quinones **1c**−**1f** (Figure 9, Figure 10).

Signals for the cyclobutanes can also be observed in the ^{13}C-NMR spectra of the irradiation products of the crystals **1b**−**1f**. The chemical shifts of the C_2-symmetric cyclobutanes (**1b**; $\delta = 41.91, 40.44$) are also different from the centrosymmetric ones (**1c**−**1f**: $\delta = 54.94-55.72$, Scheme 3. Assignment of the ^{1}H-NMR and ^{13}C-NMR signals for the compounds **5**, **6**, **7a**–**7f** and **1a**–**1f**

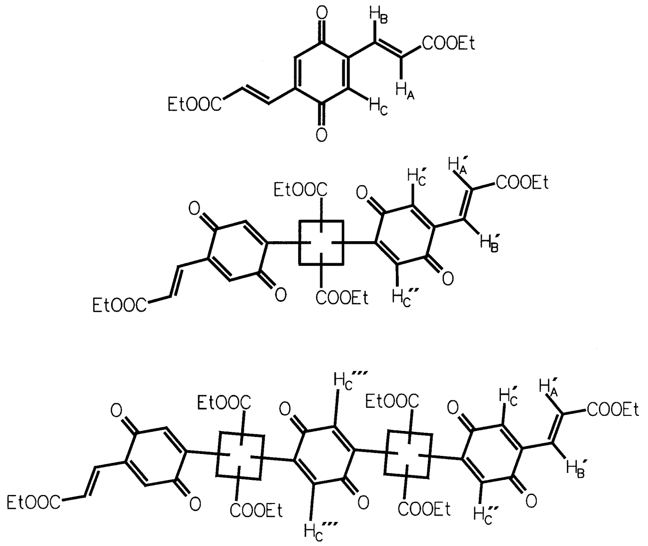
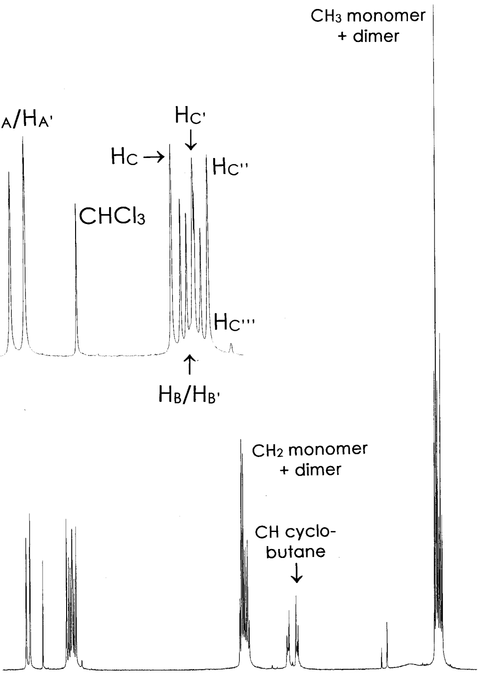


Figure 8. ^{1}H-NMR spectra of the quinone **1b** after irradiation using filter B



44.33–45.16). DEPT experiments identified the signals as of tertiary carbon atoms, thus supporting our arguments for the cycloaddition of the vinyl groups.

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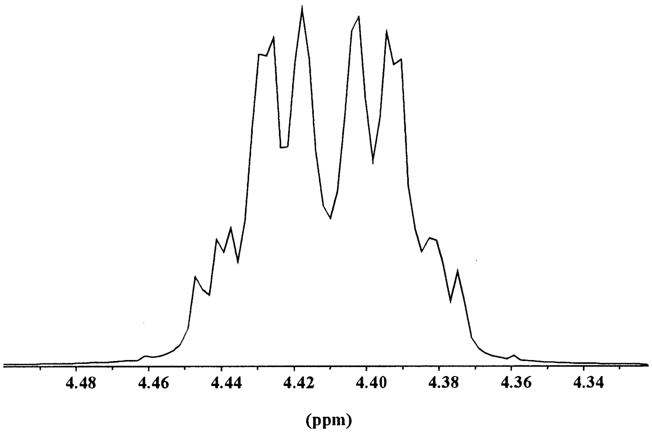
Experimental Section

Melting points: Büchi, Dr. Tottoli apparatus, open capillary tubes. – ^{1}H NMR/^{13}C NMR: Bruker AC 300 (solvent for calibration). – UV/Vis: HP 8452 A (Diode array). – Fluorescence: Jobin Yvon Spectrofluo JY 3 D. – IR: Bruker IFS 66. – MS: Finnigan 3200 for low resolutions, Vacuum Generators ZAB–2F for high resolution, Vacuum Generators ZAB–2E/70 SE for FAB spectra (matrix: *m*-nitrobenzyl alcohol with 1% trifluoroacetic acid). – Elemental analyses: Heraeus CHNO-Rapid. The spectroscopical data of new compounds are shown in Tables 4a, 4b, 5a, 5b, 6, 7, 8, 9a and 9b.

Figure 9. Simulated ^{1}H-NMR spectra of a cyclobutane ring with C_i symmetry

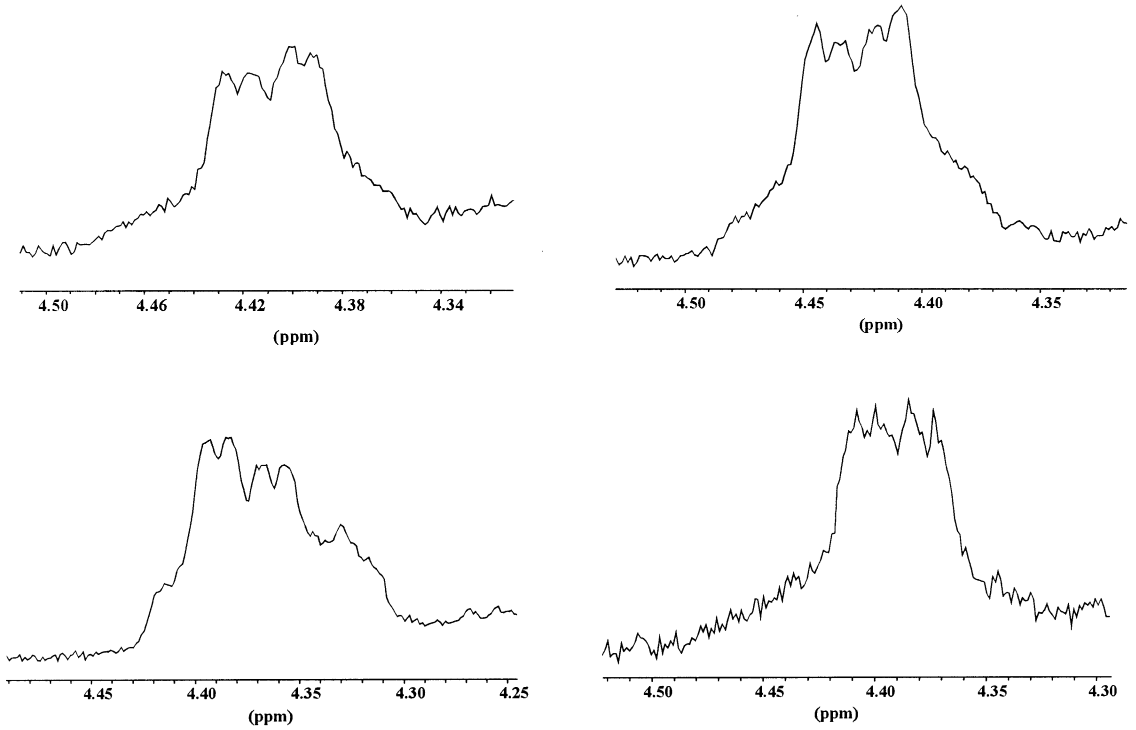


1,4-Bis(bromomethyl)-2,5-dimethoxybenzene (**3**): To a stirred solution of 150 g (1.1 mol) of 1,4-dimethoxybenzene (**2**) in 750 ml of glacial acetic acid, 65 g (2.2 mol) of paraformaldehyde and 425 ml of HBr/AcOH (40%) were added slowly. The reaction mixture was heated for 1 h at 50°C and hydrolysed in 3000 ml of water after cooling to room temperature. The residue was filtered off and suspended in 750 ml of $CHCl_3$. This suspension was refluxed for 10 min and filtered off again after cooling to room temperature. The residue was finally dried at 0.1 Torr with KOH to yield 263 g (75%) of compound **3**, m.p. 197–198°C (H_2O) [ref.[10] m.p. 196–198°C (H_2O)]. – ^{1}H NMR ($CDCl_3$): $\delta = 6.87$ (s, 2 H, arom. H), 4.54 (s, 4 H, CH_2), 3.87 (s, 6 H, CH_3).

1,4-Dimethoxy-2,5-dicarbaldehyde (**4**): To a stirred solution of 87 g (0.6 mol) of hexamethylenetetramine in 2000 ml of toluene, 100 g (0.3 mol) of compound **3** was added and refluxed for 4 h. After cooling to room temperature the yellowish salt was filtered off and dissolved in 1000 ml of $CHCl_3$. The residue was filtered off again and dried at 0.1 Torr. This salt was dissolved in 3000 ml of water. After the addition of 180 ml of formaldehyde solution (37–39%), the reaction mixture was refluxed for 3 h. After cooling to room temperature, the crude compound **4** was filtered off and purified by conversion to the bisulfite adduct. The crude product was suspended in 2000 ml of water. $Na_2S_2O_5$ (250 g, 1.3 mol) was added to the stirred suspension. The reaction mixture was refluxed for 30 min and filtered off to separate by-products. To the stirred solution of the bisulfite adduct, 600 ml (7.4 mol) of conc. HCl was added dropwise. The yellow dialdehyde **4** precipitated and was separated by filtration. Compound **4** was dissolved in 1000 ml of water, filtered off again, and dried at 0.1 Torr with P_2O_5 to yield 29.6 g (55.2%) of the terephthaldehyde **4**, m.p. 206–207°C (H_2O) [ref.[11] m.p. 206°C (H_2O)]. – ^{1}H NMR ($CDCl_3$): $\delta = 10.49$ (s, 2 H, CHO), 7.44 (s, 2 H, arom. H), 3.93 (s, 6 H, CH_3).

(E,E)-2,5-Bis(2-carboxyethenyl)-1,4-dimethoxybenzene (**5**): A stirred mixture of 20.0 g (0.1 mol) of compound **4**, 22.7 g (0.22 mol) of malonic acid, 150 ml of *N,N*-dimethylformamide (abs.), 12

Figure 10. ^{1}H-NMR signals of the cyclobutane protons after irradiation of quinone **1c** (top left), **1d** (bottom left), **1e** (top right) and **1f** (bottom right)



ml of piperidine (abs.), 2 ml of glacial acetic acid (abs.), and 2 ml of acetic anhydride (abs.) was heated at 90°C for 1 h when the emission of CO_2 ended. The reaction mixture was refluxed for 30 min. The solvents were distilled off under reduced presure. The residue was hydrolysed with 600 ml of boiling water and filtered off after cooling to room temperature. The diacid **5** was dried with P_2O_5 at 0.1 Torr to yield 28 g (96%) of a yellow powder, m.p. > 300°C (dec., H_2O). – MS (70 eV, CI, CH_4); *m/z* (%): 308 [M + $C_2H_6^+$], 307 [M + $C_2H_5^+$], 306 [M + $C_2H_4^+$], 280 [M + 2 × H^+], 279 [M + H^+], 278 [M^+], 262 [M – OH + H^+], 261 [M – OH^+], 218 [$C_{12}H_{10}O_4^+$], 217 [$C_{13}H_{13}O_3^+$], 191 [M – 2 × CO_2 + H^+].

(E,E)-2,5-Bis(2-ethoxycarbonylethenyl)-1,4-dimethoxybenzene (**6**): Compound **5** (41.1 g, 148 mmol) was suspended in a solution of 20 ml of conc. sulfuric acid in 250 ml of ethanol (abs.). The stirred reaction mixture was refluxed for 22 h. After cooling to room temperature, the residue was filtered off, washed with 600 ml of water, and dried with P_2O_5 at 0.1 Torr to yield 46.5 g (94.2%) of the yellow diester **6**, m. p. 156°C (ethanol). – MS (70 eV, EI); *m/z* (%): 334 (100) [M^+], 303 (17) [M – CH_3O^+], 289 (22) [M – $C_2H_5O^+$], 275 (44) [$C_{15}H_{15}O_5^+$], 201 (22) [$C_{12}H_9O_3^+$], 91 (17) [$C_7H_7^+$], 79 (19), 77 (17) [$C_6H_5^+$], 51 (23) [$C_4H_3^+$].

(E,E)-3,3,6,6-Tetramethoxy-1,4-bis(2-methoxycarbonylethenyl)cyclohexa-1,4-diene (**7a**): Two cylindric platinum electrodes were cleaned by heating with a burner until glowing yellow. In a beaker apparatus with planar cutting, 1.5 g (4.5 mmol) of compound **6** was suspended in a mixture of 2.0 g (36 mmol) of KOH and 500 ml of methanol (abs.). The concentrically arranged electrodes were dipped into the beaker and connected to a direct-current generator. The stirred suspension was electrolysed at 0.1–0.2 A and 4.0 V for 2.5 h. Three reaction mixtures were combined. The combined solution was concentrated to a volume of 150 ml. The oily residue was hydrolysed with 600 ml of water. The aqueous layer was extracted three times with 200 ml of ethyl acetate, stirred with NaCl and the organic layer was isolated. The combined organic layers were washed with 200 ml of brine, dried with $MgSO_4$, and concentrated to dryness. The yellowish crude product was purified by recrystallization from methanol to yield 2.9 g (59%) of the quinone bisketal (**7a**) as colourless rhombohedric plates, m.p. 198–199°C (methanol). – MS (70 eV, EI); *m/z* (%): 368 (0.1) [M^+], 353 (0.4) [M – CH_3^+], 337 (3.1) [M – CH_3O^+], 306 (2.1) [M – 2 × CH_3O^+], 305 (2.7) [$C_{16}H_{17}O_6^+$], 293 (1.3) [M – $C_3H_7O_2^+$], 275 (4.7) [$C_{15}H_{15}O_5^+$], 263 (2.8) [$C_{14}H_{15}O_5^+$], 261 (1.8) [$C_{14}H_{13}O_5^+$], 105 (100) [$C_5H_{12}O_2$ + H^+], 75 (100) [$C_3H_7O_2^+$], 59 (48) [$C_2H_3O^+$].

(E,E)-1,4-Bis(2-ethoxycarbonylethenyl)-3,3,6,6-tetramethoxycyclohexa-1,4-diene (**7b**): 1.0 g (3 mmol) of compound **7a** was stirred as a suspension in a mixture of 150 mg of tetraethyl titanate with 75 ml of ethanol (abs.) and heated at 70°C for 90 h. After removal of the solvent, the residue was again mixed with 5 drops of the catalyst and 60 ml of ethanol and heated at 70°C for 19 h. The solution was concentrated to dryness and dissolved in 100 ml of ethyl acetate. This solution was washed with 150 ml of water and the aqueous layer was extracted twice with 100 ml of ethyl acetate. The combined organic layers were washed with 100 ml of brine and dried with $MgSO_4$. After removal of the solvent, the residue was recrystallized from methanol to yield 1.0 g (97%) of the colourless ethyl ester **7b**, m.p. 145–146°C (methanol). – MS (70 eV, EI); *m/z* (%): 396 (0.8) [M^+], 381 (2.5) [M – CH_3^+], 365 (12.7) [M – CH_3O^+], 334 (5.3) [M – 2 × CH_3O^+], 319 (10) [$C_{17}H_{19}O_6^+$], 303 (4.5) [M – 3 × CH_3O^+], 291 (8.0) [$C_{15}H_{15}O_6^+$], 289 (4.7) [$C_{16}H_{17}O_5^+$], 275 (12) [$C_{15}H_{15}O_5^+$], 105 (100) [$C_5H_{12}O_2$ + H^+], 75 (62) [$C_3H_7O_2^+$], 39 (40) [$C_3H_3^+$].

(E,E)-3,3,6,6-Tetramethoxy-1,4-bis(2-n-propoxycarbonylethenyl)cyclohexa-1,4-diene (**7c**): To a stirred solution of 150 mg of tetraethyl titanate in 100 ml of *n*-propanol (abs.), 2.0 g (5.4 mmol) of the methyl ester **7a** was suspended. The reaction mixture was refluxed for 90 h and concentrated to dryness. The residue was

again refluxed for 24 h in 90 ml of *n*-propanol (abs.). After removal of the solvent, the crude product was dissolved in 100 ml of ethyl acetate and washed with 100 ml of water. The aqueous layer was extracted three times with 50 ml of ethyl acetate. The combined organic layers were washed with 100 ml of brine and dried with $MgSO_4$. After concentration to dryness, the material was purified by recrystallization from methanol to yield 2.0 g (87%) of the colourless *n*-propyl ester **7c**, m.p. 136−137°C (methanol). − MS (70 eV, EI); *m*/*z* (%): 424 (0.2) [M^+], 409 (0.4) [$M - CH_3^+$], 393 (3.5) [$M - CH_3O^+$], 333 (2.5) [$C_{18}H_{21}O_6^+$], 280 (8.1) [$C_{15}H_{20}O_5^+$], 247 (3.5) [$C_{14}H_{15}O_4^+$], 105 (90) [$C_5H_{12}O_2$+H^+], 75 (77) [$C_3H_7O_2^+$], 43 (100) [$C_3H_7^+$], 41 (52) [$C_3H_5^+$].

(E,E)-3,3,6,6-Tetramethoxy-1,4-bis(2-isopropoxycarbonylethenyl)cyclohexa-1,4-diene (**7d**): Compound **7a** (2.5 g, 6.8 mmol) was poured into a stirred solution of 150 mg of tetraethyl titanate in 100 ml of 2-propanol (abs.) and refluxed for 66 h. After removal of the solvent, the residue was again dissolved in a mixture of 150 mg of tetraethyl titanate with 100 ml of 2-propanol (abs.) and refluxed for 92 h. The solution was concentrated to dryness, dissolved in 50 ml of ethyl acetate, and washed with 100 ml of water. The aqueous layer was extracted three times with 50 ml of ethyl acetate The combined organic layers were washed with 50 ml of brine and dried with $MgSO_4$. After removal of the solvent, the crude material was recrystallized from methanol to yield 2.1 g (73%) of the colourless isopropyl ester **7d**, m.p. 198−199°C (methanol). − MS (70 eV, EI); *m*/*z* (%): 424 (0.1) [M^+], 409 (0.2) [$M - CH_3^+$], 393 (2.4) [$M - CH_3O^+$], 333 (1.8) [$C_{18}H_{21}O_6^+$], 291 (2.2) [$C_{16}H_{19}O_5^+$], 280 (10) [$C_{15}H_{20}O_5^+$], 261 (2.5) [$C_{15}H_{17}O_4^+$], 247 (6.9) [$C_{14}H_{15}O_4^+$], 105 (74) [$C_5H_{12}O_2 + H^+$], 75 (68) [$C_3H_7O_2^+$], 43 (100) [$C_3H_7^+$], 41 (30) [$C_3H_5^+$].

(E,E)-1,4-Bis(n-butoxycarbonylethenyl)-3,3,6,6-tetramethoxycyclohexa-1,4-diene (**7e**): In a flame-dried vessel, 0.85 g (11.5 mmol) of *n*-butanol was dissolved in 25 ml of THF (abs.) under nitrogen. This mixture was vigorously stirred. A solution of *n*-BuLi in *n*-hexane (1.6 M, 7.5 ml, 12 mmol) was added in portions with a syringe at −5°C. Methyl ester **7a** (2.0 g, 5.4 mmol) was dissolved in 90 ml of THF (abs.) and poured dropwise into the reaction mixture. The temperature was kept at 0°C for 45 min and then the cooling bath was removed. After 70 h, 1.0 g of *n*-butanol and 5 ml of the BuLi solution were added and the stirring process was continued for 6 h. The reaction mixture was hydrolysed in 600 ml of water. The aqueous layer was extracted with 200 ml of ethyl acetate. The combined organic layers were washed with 100 ml of brine, and dried with $MgSO_4$. The solution was concentrated to dryness and the residue was recrystallized from methanol to yield 1.2 g (49%) of the *n*-butyl ester **7e**, m.p. 128−129°C. − MS (70 eV, EI); *m*/*z* (%): 452 (0.5) [M^+], 437 (0.9) [$M - CH_3^+$], 421 (6.3) [$M - CH_3O^+$], 390 (3.0) [$M - 2 \times CH_3O^+$], 347 (3.6) [$C_{19}H_{23}O_6^+$], 294 (5.5) [$C_{16}H_{22}O_5^+$], 105 (100) [$C_5H_{12}O_2 + H^+$], 75 (94) [$C_3H_7O_2^+$], 57 (28) [$C_4H_9^+$], 41 (53) [$C_3H_5^+$].

(E,E)-1,4-Bis(benzyloxycarbonylethenyl)-3,3,6,6-tetramethoxycyclohexa-1,4-diene (**7f**): A solution of 1.8 g (14 mmol) of benzyl alcohol in 20 ml of THF (abs.) was poured into a flame-dried vessel. A solution of *n*-BuLi in *n*-hexane (15%, 10.0 ml, 16 mmol) was added dropwise with a syringe at −5°C. Compound **7a** (1.5 g, 4.1 mmol) was dissolved in 100 ml of THF (abs.) and poured slowly into the reaction mixture. The cooling bath was removed and the contents of the vessel were stirred for a further 6.5 h. The solution was hydrolysed in 500 ml of water. The organic material was extracted with 200 ml of ethyl acetate, the aqueous layer was stirred with NaCl and the organic layer was isolated. The combined organic layers were washed with 100 ml of brine and dried with $MgSO_4$. The solvent was removed and the oily residue was recrystallized from methanol to yield a white powder. It contained the quinone bisketal **7a** and **7f**. To obtain the pure benzyl ester **7f** it was necessary to repeat this procedure with the mixture of the esters, using 3.0 g (28 mmol) of benzyl alcohol and 7.0 ml (11 mmol) of a solution of *n*BuLi. The mixture of the esters was dissolved in 10 ml of THF (abs.). After 2 h, 120 ml of water was added and the organic material was extracted with 50 ml of ethyl acetate. This solution was treated, as described, to yield 450 mg (21.1%) of the benzyl ester **7f**, m.p. 156−157°C (methanol). − MS (70 eV, EI); *m*/*z* (%): 520 (0.1) [M^+], 489 (0.6) [$M - CH_3O^+$], 429 (0.4) [$M - C_7H_7^+$], 328 (6.4) [$C_{19}H_{20}O_5^+$], 237 (3.3) [$C_{12}H_{13}O_5^+$], 219 (4.6) [$C_{12}H_{11}O_4^+$], 105 (100) [$C_5H_{12}O_2 + H^+$], 92 (47) [$C_7H_8^+$], 91 (100) [$C_7H_7^+$], 75 (100) [$C_3H_7O_2^+$], 65 (29) [$C_5H_5^+$].

All quinone bisketals **7a**−**7f** have to be stored under an atmosphere of dry ammonia.

General Procedure for the Synthesis of the Quinones **1a**−**1f**: To a solution of the quinone bisketals, 1−3 drops of sulfuric acid (0.2 N) were added (Table 3). All solutions turned yellow. After 16 h, the quinones were precipitated and filtered off to yield yellow crystals. These crystals were purified by recrystallization from acetone.

Table 3. Synthesis of the quinones **1a**−**1f**

	ketal amount		solvent acetone		quinone amount	yield
	[g]	[mmol]	[ml]		[g]	[%]
7a	0.5	1.36	20	**1a**	0.37	99
7b	0.1	0.25	3 (+ 3 ml of CH_2Cl_2)	**1b**	0.07	94
7c	1.0	2.36	25	**1c**	0.65	83
7d	1.0	2.36	50	**1d**	0.63	80
7e	0.71	1.47	40	**1e**	0.43	76
7f	0.25	0.48	10	**1f**	0.10	48

Table 4a. ^{1}H-NMR data of compounds **5**, **6**, **7a**−**7f**; hydrogen atoms: (a) methoxy; (b) ring; (c) vinyl (ring); (d) vinyl (ester); (e) carboxylic acid of **8**; (f)−(i) CH_2 and CH_3 groups of the ester

	^{1}H-NMR peaks (δ)							
atom	**5**	**6**	**7a**	**7b**	**7c**	**7d**	**7e**	**7f**
(a)	3.87	3.86	3.19	3.20	3.20	3.18	3.18	3.19
(b)	7.37	7.01	6.35	6.36	6.36	6.34	6.34	6.36
(c)	7.81	7.93	6.62	6.62	6.63	6.57	6.61	6.68
(d)	6.68	6.53	7.23	7.23	7.23	7.18	7.20	7.26
(e)	12.1−12.7	–	–	–	–	–	–	–
(f)	–	4.26	3.77	4.23	4.13	5.07	4.15	5.22
(g)	–	1.34	–	1.31	1.70	1.26	1.65	–
(h)	–	–	–	–	0.97	–	1.39	–
(i)	–	–	–	–	–	–	0.93	–
arom.	–	–	–	–	–	–	–	7.33−7.42

Table 4b. ^{1}H-NMR data of the quinones **1a**−**1f**; assignment of the hydrogen atoms as in Table 4a

	^{1}H-NMR peaks (δ)					
atom	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**
(b)	7.03	6.91	6.91	6.90	6.90	6.89
(c)	6.47	6.85	6.85	6.83	6.85	6.91
(d)	7.77	7.49	7.48	7.47	7.47	7.52
(f)	3.72	4.27	4.16	5.13	4.20	5.25
(g)	–	1.33	1.72	1.31	1.66	–
(h)	–	–	0.97	–	1.41	–
(i)	–	–	–	–	0.94	–
arom.	–	–	–	–	–	7.36−7.39

(E,E)-2,5-Bis(2-methoxycarbonylethenyl)-1,4-benzoquinone (**1a**): M.p. > 250°C (acetone, dec.). − MS (70 eV, EI); *m/z* (%): 278 (0.2) $[M + 2 \times H^+]$, 246 (0.5) $[M - CH_2O^+]$, 245 (2.6) $[M - CH_3O^+]$, 217 (13) $[C_{12}H_9O_4^+]$, 158 (29) $[C_{10}H_6O_2^+]$, 102 (19) $[C_8H_6^+]$, 79 (75) $[C_5H_3O^+]$, 59 (100) $[COOCH_3^+]$, 51 (100) $[C_4H_3^+]$.

Table 5a. ^{13}C-NMR data of **5**, **6**, **7a**−**7f**; carbon atoms: (a) methoxy; (b) C(−O) (ring); (c) C(−C) (ring); (d) C(−H) (ring); (e) vinyl C (ring); (f) vinyl C (ester); (g) carbonyl C; (h)−(l) CH_2 and CH_3 groups of the ester; (m)−(p) phenyl C of benzyl groups of **7f**

	^{13}C-NMR peaks (δ)							
atom	**5**	**6**	**7a**	**7b**	**7c**	**7d**	**7e**	**7f**
(a)	56.24	56.03	50.95	50.98	51.01	51.01	51.01	51.04
(b)	151.87	152.49	95.92	95.96	95.99	95.97	95.99	95.95
(c)	125.24	125.96	138.76	138.82	138.85	138.58	138.57	138.78
(d)	111.14	111.08	135.96	135.94	135.90	136.07	135.94	136.29
(e)	137.63	138.99	122.87	123.33	123.34	123.81	123.35	123.05
(f)	120.66	119.88	139.10	138.85	138.95	138.85	138.84	139.46
(g)	167.69	167.11	167.26	166.85	166.98	166.39	166.99	166.74
(h)	−	60.66	51.66	60.57	66.27	67.96	64.54	66.51
(i)	−	14.33	−	14.23	22.03	21.86	30.72	−
(k)	−	−	−	−	10.41	−	19.15	−
(l)	−	−	−	−	−	−	13.69	−
(m)	−	−	−	−	−	−	−	135.92
(n)	−	−	−	−	−	−	−	128.31
(o)	−	−	−	−	−	−	−	128.57
(p)	−	−	−	−	−	−	−	128.42

Table 5b. ^{13}C-NMR data of the quinones **1a**−**1f**; assignment of the carbon atoms as in Table 5a

	^{13}C-NMR peaks (δ)				
atom	**1b**	**1c**	**1d**	**1e**	**1f**
(b)	185.67	185.66	185.72	185.68	185.70
(c)	134.72	134.70	134.43	134.71	135.42
(d)	133.69	133.70	133.58	133.71	134.07
(e)	128.42	128.38	128.94	128.43	128.52
(f)	139.73	139.66	139.81	139.71	139.70
(g)	165.51	165.59	165.04	165.61	165.48
(h)	61.16	66.74	68.75	65.06	67.10
(i)	14.18	21.93	21.81	30.63	−
(k)	−	10.33	−	19.12	−
(l)	−	−	−	13.65	−
(m)	−	−	−	−	135.61
(n)	−	−	−	−	128.25
(o)	−	−	−	−	128.78
(p)	−	−	−	−	128.61

Table 6. UV absorption and fluorescence emission of the compounds **5**, **6**, **7a**−**7f**, **8**, **1a**−**1f**

comp.	UV absorption λ [nm]						fluorescence emission λ [nm]
5	210	240 (sh)		306	380		576
6		244 (sh)		310	392		458
7a			252				−
7b			252				−
7c			252				−
7d			252				−
7e			252				−
7f			254				−
8			256	314	376	400	476
1a			254	310	360 (sh)		−
1b			256	310	362 (sh)	450	−
1c			256	310	362 (sh)	458	−
1d			254	308	368 (sh)	480	−
1e			256	310	360 (sh)	442	−
1f			256	306	364 (sh)	472	−

(E,E)-2,5-Bis(2-ethoxycarbonylethenyl)-1,4-benzoquinone (**1b**): M.p. > 163°C (acetone, dec.). − MS (70 eV, EI); *m/z* (%): 306 (0.2) $[M + 2 \times H^+]$, 259 (4.9) $[M - C_2H_5O^+]$, 159 (45) $[C_9H_3O_3^+]$, 158 (58) $[C_9H_2O_3^+]$, 102 (32) $[C_7H_2O^+]$, 79 (83) $[C_5H_3O^+]$, 51 (100) $[C_4H_3^+]$.

(E,E)-2,5-Bis(2-n-propoxycarbonylethenyl)-1,4-benzoquinone (**1c**): M.p. 162−163°C (acetone, dec.). − MS (70 eV, EI); *m/z* (%): 334 (2.2) $[M + 2 \times H^+]$, 275 (4.0) $[M + 2 \times H - C_3H_7O^+]$, 215 (10) $[C_{12}H_7O_4^+]$, 214 (57) $[C_{12}H_6O_4^+]$, 43 (100) $[C_3H_7^+]$.

Table 7. IR-spectroscopical data of the compounds **5**, **6**, **7a**−**7f**, **8**, **1a**−**1f**

comp.	stretching bonds $\tilde{\nu}$ [cm^{-1}]							
	C=O (ester)	C=O (quinone)	C=C (quinone)	C=C (olef.)		C−O−C (ether, ketal)		
5	1693	−	−	1615		1282	1210	1043
6	1715	−	−	1633	1272	1216	1180	1080
7a	1711	−	1636	1619	1319	1305	1175	1059
7b	1717	−	1635	1613	1318	1296	1184	1058
7c	1713	−	1635	1617	1319	1298	1179	1065
7d	1704	−	1634	1617	1315	1304	1182	1061
7e	1708	−	1634	1617	1307		1175	1064
7f	1708	−	1631	1614	1314		1188	1084
8	1704	1667	1629	1586	1369	1306	1183	1049
1a	1704	1666	1620	1600	−	−	−	−
1b	1707	1666	1624	1567	−	−	−	−
1c	1708	1669	1621	1568	−	−	−	−
1d	1706	1669	1623	1569	−	−	−	−
1e	1707	1668	1622	1568	−	−	−	−
1f	1709	1663	1626	1569	−	−	−	−

Table 8. Elemental analysis of the compounds **5**, **6**, **7a**−**7f**, **8**, **1a**−**1e**

comp.	mol mass [g]	C calcd.	C found	H calcd.	H found	O calcd.	O found
5	278.26	60.43	60.33	5.07	5.17	34.50	34.50
6	334.34	64.66	64.52	6.63	6.50	28.71	28.98
7a	368.38	58.69	58.74	6.56	6.63	34.75	34.63
7b	396.44	60.59	60.34	7.12	7.10	32.29	32.56
7c	424.49	62.25	62.51	7.60	7.56	30.15	29.93
7d	424.49	62.25	62.26	7.60	7.59	30.15	30.15
7e	452.55	63.70	63.59	8.02	7.94	28.28	28.47
7f	520.58	69.22	68.80	6.19	6.26	24.59	24.94
8	350.37	61.71	61.49	6.32	6.30	31.97	32.21
1a	276.25	60.87	60.70	4.38	4.40	34.75	34.90
1b	304.30	63.15	63.35	5.30	5.38	31.55	31.27
1c	332.35	65.05	64.92	6.07	6.17	28.88	28.91
1d	332.35	65.05	64.86	6.07	6.12	28.88	29.02
1e	360.41	66.65	66.53	6.71	6.76	26.64	26.71

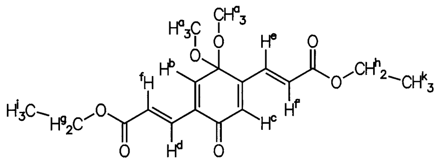
(E,E)-2,5-Bis(2-isopropoxycarbonylethenyl)-1,4-benzoquinone (**1d**): M.p. > 195°C (acetone, dec.). − MS (70 eV, EI); *m/z* (%): 334 (0.2) $[M + 2 \times H^+]$, 274 (1.5) $[M + H - C_3H_7O^+]$, 273 (8.0) $[M - C_3H_7O^+]$, 245 (2.5) $[C_{13}H_9O_5^+]$, 214 (3.2) $[M - 2 \times C_3H_7O^+]$, 187 (4.3) $[C_{10}H_3O_4^+]$, 186 (16) $[C_{10}H_2O_4^+]$, 158 (19) $[C_9H_2O_3^+]$, 79 (40) $[C_5H_3O^+]$, 51 (46) $[C_4H_3^+]$, 43 (100) $[C_3H_7^+]$, 41 (80) $[C_3H_5^+]$.

(E,E)-2,5-Bis(2-n-butoxycarbonylethenyl)-1,4-benzoquinone (**1e**): M. p. 175−176°C (acetone, dec.). − MS (70 eV, CI, CH_4); *m/z* (%): 403 $[M + C_3H_7^+]$, 402 $[M + C_3H_6^+]$, 401 $[M + C_3H_5^+]$, 390 $[M + C_2H_6^+]$, 389 $[M + C_2H_5^+]$, 362 $[M + 2 \times H^+]$, 361 $[M + H^+]$, 360 $[M^+]$, 307 $[M - C_4H_7 + 2 \times H^+]$, 306 $[M - C_4H_7 + H^+]$, 305 $[M - C_4H_7^+]$, 289 $[M - C_4H_9 + 2 \times H^+]$, 288 $[M - C_4H_9 + H^+]$, 287 $[M - C_4H_9^+]$, 261 $[C_{15}H_{15}O_4 + 2 \times H^+]$, 260 $[C_{15}H_{15}O_4 + H^+]$, 259 $[C_{15}H_{15}O_4^+]$ 206 $[C_{11}H_8O_4 + 2 \times H^+]$, 205 $[C_{11}H_8O_4 + H^+]$.

(E,E)-2,5-Bis(2-benzyloxycarbonylethenyl)-1,4-benzoquinone (**1f**): M. p. > 148°C (acetone, dec.). − MS (70 eV, EI, high resolution): $C_{26}H_{22}O_6$: calcd. 430.1416; found 430.1393.

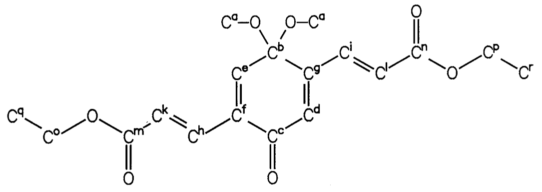
(E,E)-1,4-Bis(2-ethoxycarbonylethenyl)-3,3-dimethoxy-6-oxocyclohexa-1,4-diene (**8**): To a solution of 0.5 g (1.4 mmol) of the quinone bisketal **7b** in 10 ml of DMF (abs.), 1 drop of sulfuric acid (2 N) was added. The solution was stirred for 16 h at 5°C, for 24 h at −30°C, and for 7 d at −64°C. After warming up to room temperature, 3 ml of water was added. After storing for 3 d at 5°C, crystals precipitated to yield 110 mg (24.2%) of the monoketal **8**, m.p. 97.5−98.5°C (H_2O/DMF). − MS (70 eV, EI); *m/z* (%): 351 (5) [M^+], 350 (23) [M^+], 322 (22) [M − CO^+], 305 (42) [M − $C_2H_5O^+$], 261 (40) [$C_{14}H_{13}O_5^+$], 246 (28) [$C_{13}H_{10}O_5^+$], 215 (19), 201 (100) [$C_{11}H_5O_4^+$], 158 (31) [$C_9H_2O_3^+$], 131 (26), 79 (31), 51 (30) [$C_4H_3^+$].

Table 9a. ^{1}H-NMR data of the quinone monoketal **8**



atom	a	b	c	d	e	f/f′	g	h	i	k
δ	3.21	6.53	6.94	7.38	6.78	7.25	4.23	4.22	1.30	1.29

Table 9b. ^{13}C-NMR data of the quinone monoketal **8**



atom	a	b	c	d	e	f	g	h	i
δ	51.24	95.89	183.49	132.48	136.21	135.92	148.80	127.53	124.59

atom	k	l	m	n	o	p	q	r
δ	143.96	137.43	166.30	166.01	60.94	60.75	14.21	14.18

X-ray Diffraction Analysis: Data collection was carried out with an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation and ω/2Θ scan with Θ = 2−28°. Structure solution and refinement were performed with a Microvax 3100 (program: MolEN[12]). More details on the structure determination are given in Table 10[13]. For *(E,E)*-2,5-bis(2-ethoxycarbonylethenyl)-1,4-dimethoxybenzene (**6**), *(E,E)*-1,4-bis(2-ethoxycarbonylethenyl)-3,3-dimethoxy-6-oxocyclohexa-1,4-diene (**8**) and *(E,E)*-2,5-bis(2-ethoxycarbonylethenyl)-1,4-benzoquinone (**1b**) the coordinates of the hydrogen atoms and their thermal parameters were fixed during refinement. One of the ethyl groups from compound (**8**) was disordered (50%). These four carbon atoms were isotropically refined. Because of extinction effects and the large irregularities in the lattice of compound **1b**, 19 reflections were excluded from the refinement process.

Irradiation of the Quinones **1a**−**1f**: All irradiations were carried out with a 1200-W high-pressure mercury lamp (Q 1200, Heraeus, Hanau). The powdered quinones were dispersed homogenously in a dish made of aluminium foil and covered with the appropriate filter. Filter A (Schott KV 370) absorbs light with λ ≤ 370 and filter B (Schott KV 520) with λ ≤ 520 nm. All quinones were irradiated successively under dried nitrogen for 4 h at 20°C. After 60, 120 and 180 min, the irradiated probes were mixed well. More details can be obtained in ref.[15]. The irradiated probes were investigated by ^{1}H-NMR, ^{13}C-NMR, IR and FAB-MS studies (Table 11 and Table 12). The NMR spectra of the irradiated quinone **1b** (filter B) could be interpreted in detail.

1b: ^{1}H NMR ($CDCl_3$): δ = 7.483 (d, ^3J = 16.2 Hz, monom.), 7.480 (d, ^3J = 16.2 Hz, dim.), 6.90 (s, 0.88 H, monom.), 6.84 (d, ^3J = 16.2 Hz, monom.), 6.819 (s, dim.), 6.817 (d ^3J = 16.2 Hz, 0.84 H, dim.), 6.76 (s, 0.4 H, dim.), 6.677 (s, 0.03 H, trim.), 4.26 (q, ^3J = 7.11 Hz, 3.1 H, monom.), 4.19 (q, ^3J = 7.23 Hz, 1.96 H, dim.), 3.58−3.42 (m, AA′BB′, 2 H, dim.), 1.32 (t, ^3J = 6.99 Hz, 5.22 H, monom.), 1.25 (t, ^3J = 7.17 Hz, 3.1 H, dim.). − ^{13}C NMR ($CDCl_3$): δ = 186.49 (dim.), 185.68 (monom.), 185.64 (dim.),

Table 10. Experimental details of the X-ray diffraction analysis and refinement

compound	**6**	**7a**	**8**	**1b**
crystal size [mm]	0.1 × 0.15 × 0.4	0.15 × 0.25 × 0.25	0.15 × 0.15 × 0.15	0.5 × 0.16 × 0.14
crystal form	yellow needles	colourless prisms	yellow plates	yellow needles
cystal growing	ethanol	acetone	DMF/water	acetone
T [K]	293	293	293	243
space group	*C*2/c	$P\bar{1}$	$P2_1/c$	*Cmca*
Z	4	1	4	4
reflections:				
recorded	2120	2478	4752	992
unique	2073	2288	4497	992
observed [$I > 2.5\sigma(I)$]	866	1236	1577	336
R_{int}	0.045	0.031	0.017	−
number of variables	109	154	224	67
solution method[16][17]	SHELXS-86	SHELXS-86	MULTAN	SHELXS-86
refined on	F^2	F^2	F^2	F^2
μ [m^{-1}]	90.1	93.9	89.0	100
$(\Delta\rho)_{max}$ [eÅ^{-3}]	0.224	0.196	0.245	0.34
$(\Delta\rho)_{min}$ [eÅ^{-3}]	−0.214	−0.280	−0.221	−0.21
R	0.044	0.045	0.053	0.094
R_w (*F*)	0.052	0.054	0.066	0.108

Table 11. Ratio of the $C=C$ (vinyl) to the $C=C$ (quinone) IR intensities before and after irradiation of quinone crystals **1a**−**1f**; 4 h, 20°C; filter A: 405−579nm; filter B: 546−579 nm

quinone	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**
before irradiation	1.3	1.8	1.2	1.1	1.1	1.0
filter A	1.1	0.3	0.2	0.9	0.3	0.4
filter B	1.1	0.3	0.1	0.3	0.3	0.3

Table 12. Relative intensities of FAB-MS peaks of the quinones **1a**−**1f** and their irradiation products (filters A and B). n = 1: monomer; n = 2−7: oligomer

quinone		relative intensities [%]						
		$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$
1a	before irradiation	100	4					
	filter A	100	24	5				
	filter B	100	6					
1b	before irradiation	100	17	1				
	filter A	100	57	25				
	filter B	100	62	18	11	6	4	
1c	before irradiation	645	100	16				
	filter A	0	100	49	18	8	4	1
	filter B	0	100	44	20	9	5	
1d	before irradiation	1333	100	23				
	filter A	0	100	54	41	36		
	filter B	0	100	59	24	10	5	
1e	before irradiation	699	100					
	filter A	0	100	53	21	9	8	
	filter B	0	100	57	27	12	15	
1f	before irradiation	100	11					
	filter A	100	144	38	16	5	4	
	filter B	100	83	28	13	7		

170.82 (dim.), 165.57 (dim.), 165.53 (monom.), 146.66 (dim.), 139.73 (monom.), 139.66 (dim.), 134.91 (dim.), 134.73 (monom.), 133.69 (monom.), 133.31 (dim.), 132.56 (dim.), 128.41 (monom.), 128.24 (dim.), 61.58 (dim.), 61.16 (monom.), 61.13 (dim.), 41.94 (dim.), 40.45 (dim.), 14.18 (monom. + dim.), 14.14 (dim.).

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☆ Dedicated to Professor *Gottfried Huttner* on the occasion of his 60th birthday.