

Multichromophoric Systems by Diels–Alder Reaction of Barrelene with *o*-Benzoquinones: Tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-9,11,13-triene-4,5-diones[☆]

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Thermal addition of *o*-benzoquinones to barrelenes (bicyclo[2.2.2]octatrienes) produces tetracyclic trienediones of type **1**. These multichromophoric molecules offer a plethora of photochemical reactions of which the most interesting are (1) rearrangement and bisdecarbonylation of the enedione chromophore and (2) $[2\pi + 2\pi]$ intramolecular

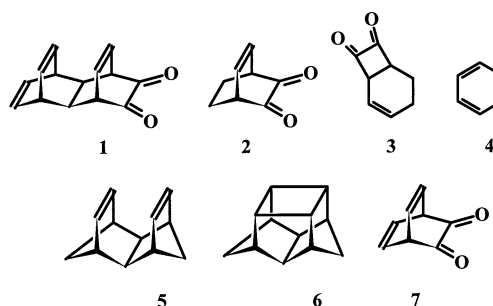
cycloaddition of the face-to-face double bonds. Theoretical methods (semiempirical as well as density functional) were also used to investigate the spin multiplicity diversity of these reactions. The diketone **7** (bicyclo[2.2.2]octa-5,7-diene-2,3-dione) was investigated using He(I) photoelectron spectroscopy.

Introduction

Rearrangements and bisdecarbonylations of enedione chromophores^[1] (type 1) and $[2\pi + 2\pi]$ intramolecular cycloadditions^[2] of face-to-face double bonds (type 2) are well-known photoreactions. Reactions of type 1 have been observed with a variety of simpler enediones (e.g. **2**) and have been of synthetic utility^[1]. The lowest singlet states of such enediones react with moderate efficiency ($\phi = 0.1–0.5$) through allylic rearrangement, an 1,3-acyl shift, to give unsaturated cyclobutanediones (e.g. **3**) while the triplet state undergoes bisdecarbonylation with higher efficiency ($\phi = 0.5–1.0$) to give conjugated dienes (e.g. **4**). Some derivatives of **2** possessing an unsubstituted enedione chromophore behave in a more complicated fashion and undergo competing rearrangement and bisdecarbonylation upon direct irradiation; such reactions exhibit concentration and temperature dependence^[3]. The unsaturated cyclobutanedione **3** also undergoes photochemical bisdecarbonylation to **4** through both singlet and triplet pathways; here again the triplet reaction is more efficient than the singlet one. While **2** is thermally stable (recovered unchanged after heating at 150 °C), **3** undergoes competing rearrangement back to **2** and bisdecarbonylation to **4** at moderate temperatures^[4].

Reactions of type 2, i.e. intramolecular cycloadditions to give cyclobutane derivatives, have been of considerable interest. A compound closely related to **1** is the diene **5**, and

Scheme 1



its photocycloaddition to give the cage product **6** has been studied in detail by Jones and coworkers^[5]. Direct irradiation (254 nm, $\phi = 0.5$) and triplet-sensitized reaction (benzophenone, 366 nm, $\phi = 1$) of **5** resulted in exclusive formation of cage compound **6**. In addition, irradiation in polar solvents (e.g. acetonitrile) in the presence of electron-acceptor sensitizers (e.g. 2-cyanonaphthalene) resulted in the formation of **6** with quantum yields greater than unity. It was suggested that this process involves short chains with single electron transfer (SET) from the ground state diene to the singlet excited sensitizer as the initial step. Exciplex formation was proposed for the same sensitizer reactions in non-polar solvents and charge-transfer complex formation for reactions with strong acceptors like fumaronitrile. We

note that the electron affinity of biacetyl^[6] ($EA = 0.72$ eV) is close to that of 2-cyanonaphthalene^[7] ($EA = 0.68$ eV), suggesting that an intramolecular SET mechanism could conceivably occur with multichromophoric molecules containing both the homoconjugated diene fragment and an α -dicarbonyl unit, e.g. **1**. It should also be noted that non-bonded distances between the carbon atoms of the face-to-face double bonds, measured by X-ray crystallographic analysis of four chlorosubstituted compounds^[8] related to **5**, are all very close to the range of 2.9–3.1 Å expected for **1**. Additional possibilities for photochemical reactions for multichromophores of type **1** include di- π -methane reaction of homoallylic double bonds and oxa-di- π -methane reaction between carbonyl and alkene groups^[9].

We report the synthesis of **1**, a study of the direct and triplet sensitized photoreactions of **1** as well as results of theoretical calculations. The retro Diels–Alder reaction of an α,p' -dibenzene derivative (the systematic name of α,p' -dibenzene is: 1,4-etheno-1,4,4a,8a-tetrahydronaphthalene) obtained in the present work is also presented.

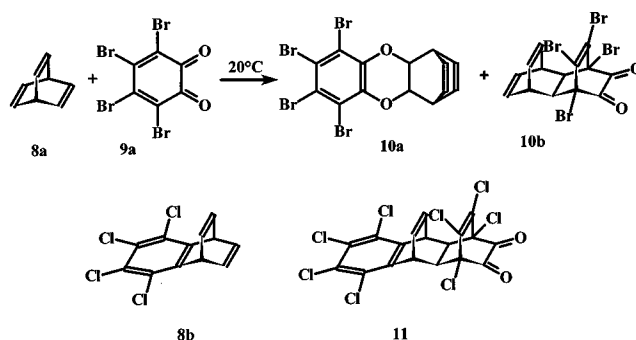
Results and Discussion

Synthesis

Cycloaddition between barrelene **8a** (bicyclo[2.2.2]octatriene) and α -benzoquinone **9b** was performed at room temperature in THF solution. Due to the instability of the quinone, fresh portions were added daily over a ten-day period. The yellow crystalline product **1** was isolated in about 10% yield by chromatography on silica gel. Its structure assignment is based on elemental composition and spectroscopic properties as presented in the Experimental Section. Thermolysis of **1** (140°C, 4 min) produced bicyclo[2.2.2]-5,7-diene-2,3-dione (**7**)^[10], providing a convenient alternative synthesis^{[10][11]} for **7** as well as further confirmation of the structure assignment for **1**. The quinoxaline of **1** has been described previously^[12].

It was hoped that this Diels–Alder reaction with inverse electron demand might be general and could be used to prepare a variety of substituted derivatives of **1**. However, attempts to prepare analogous adducts of barrelene with other α -quinones met with very limited success. No reaction was observed when alkyl-substituted quinones were used. Tetrachloro- α -benzoquinone with barrelene afforded exclusive hetero Diels–Alder addition to give a carbonyl-free dioxene, but tetrabromo- α -benzoquinone (**9a**) with barrelene **8a** produced a mixture of the hetero Diels–Alder product **10a** as well as the desired diketone **10b**. Reaction between tetrachlorobenzobarrelene (**8b**) and tetrachloro- α -benzoquinone also proceeded as desired to give the diketone **11** in 64% yield. Because of these synthetic limitations, it was not possible to perform a systematic study on the effect of substituents on the photochemistry or on the retro Diels–Alder reactions of α,p' -dibenzene derivatives obtained by bisdecarbonylation of diketones.

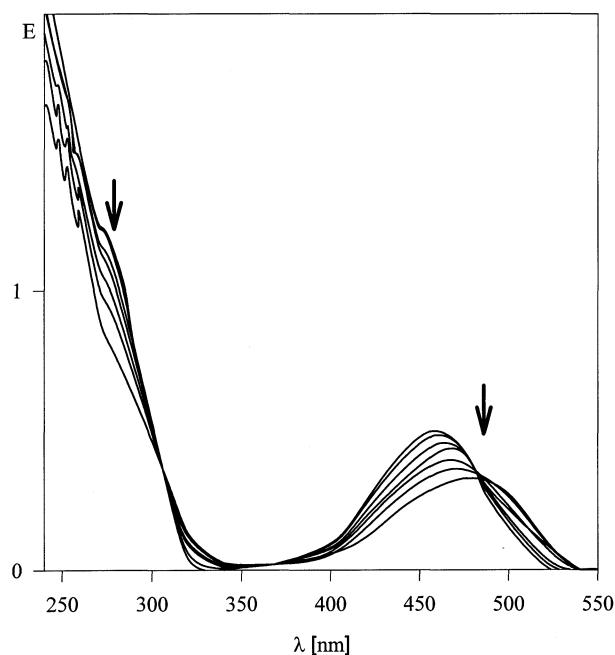
Scheme 2



Direct Photolysis

The spectroscopic changes observed upon room temperature irradiation of **1** in dry methylcyclohexane (MCH) at 436 nm are shown in Figure 1.

Figure 1. Spectroscopic changes upon room-temperature irradiation of **1** (1.3 mg/3 ml of MCH) at 436 nm; the arrows indicate the direction of changes; isosbestic points were observed at early stages of the irradiation but isosbestic behavior did not persist as the irradiation was continued



Isosbestic points were observed at 305, 374, and 482 nm at early stages of the irradiation. The new, long-wavelength maximum appearing in these irradiations is assigned to the rearrangement product, cyclobutanedione derivative **12**. Isosbestic behavior did not persist as the irradiation was continued and new, more intense maxima were observed at 243, 249, 254, and 261 nm. These were identified as the absorptions of benzene. Exhaustive irradiation to a constant ratio of absorbance at 436 and 496 nm resulted in a considerable degree of benzene formation and the appearance of the long-wavelength maximum of product **12** at 496 nm. The molar extinction coefficient for **12** at its maximum was calculated to be 110, and at 436 nm the extinction coef-

ficient was 36. This significant absorption at the irradiating wavelength, plus the higher quantum yield ($\phi_{-12} = 0.24$, see below) for bisdecarbonylation of **12**, explains why the isosbestic behavior did not persist in the later stages of reaction. Irradiation of **1** at 254 nm under otherwise identical conditions resulted in direct formation of benzene without detectable isomerization to **12**.

When the irradiation was performed at 436 nm in a mixture of dichloromethane and MCH in an IR cell, new bands were observed at 1770 and 1795 cm^{-1} , which are characteristic of the cyclobutanedione chromophore^{[1][13]}.

Heating an MCH solution of **12** at 65 °C for 3.25 h resulted in the formation of benzene (76%) and regeneration of **1** (24%) based on UV and ¹H-NMR spectroscopy. Similar isomerizations of allylic cyclobutanediones have been observed previously in a number of cases with varying ratios between decarbonylation and rearrangement products^[4].

Irradiations of **1** were normally performed in sealed, degassed cuvettes because of the extreme sensitivity of **12** to moisture. However, it was shown that the quantum yield of the isomerization **1** → **12** was not affected by the presence of air nor by added anthracene. These results, together with the isosbestic behavior, are consistent with a singlet-state reaction proceeding specifically to cyclobutanedione **12**.

Quantum yields for the disappearance of **1** showed marked temperature and concentration dependence. At concentrations lower than about $2 \cdot 10^{-3}$ M, quantum yields for both the disappearance of **1** (ϕ_{-1}) and for the formation of **12** (ϕ_{12}) were 0.10. At higher concentrations, ϕ_{-1} remained 0.10, but ϕ_{12} decreased with increasing concentration of **1**. The results are summarized in Table 1.

Table 1. Concentration dependence of quantum yields at 436 nm for reaction of **1** in methylcyclohexane (MCH) at room temperature

molarity [10^{-3} M]	ϕ_{-1} ^[a]	ϕ_{12} ^[b]
0.91	0.10	0.11
2.80	0.11	0.07
4.32	0.10	0.05
7.10	0.10	0.04
9.56	0.11	0.03

^[a] Quantum yield for the disappearance of **1** determined by the decrease in absorption at 456 nm (corrected for absorption of **12**).
^[b] Quantum yield for the formation of **12** determined from the absorption at 496 nm using $\varepsilon = 110$.

Similar behavior has been observed with a number of diketones that are unsubstituted on the cyclohexenedione chromophore and studied in detail with bicyclo[2.2.2]oct-5-ene-2,3-dione^[3]. In that study this behavior has been attributed to excimer formation and the availability of new decay routes.

The reaction also showed a temperature dependence; quantum yield data are summarized in Table 2, best conversions to **12** were achieved at 50 °C.

Table 2. Temperature dependence of quantum yields for reaction of $1.88 \cdot 10^{-3}$ M of **1** in MCH/CH₂Cl₂ (9:1, v/v) at 436 nm

<i>T</i> [K]	ϕ_{-1} ^[a]	ϕ_{12} ^[b]
298	0.10	0.10
268	0.052	0.035
243	0.054	0.00
218	0.013	0.00
193	0.01	0.00

^[a] Quantum yield for the disappearance of **1** determined by the decrease in absorption at 456 nm (corrected for absorption of **12**).
^[b] Quantum yield for the formation of **12** determined from the absorption at 496 nm using $\varepsilon = 110$.

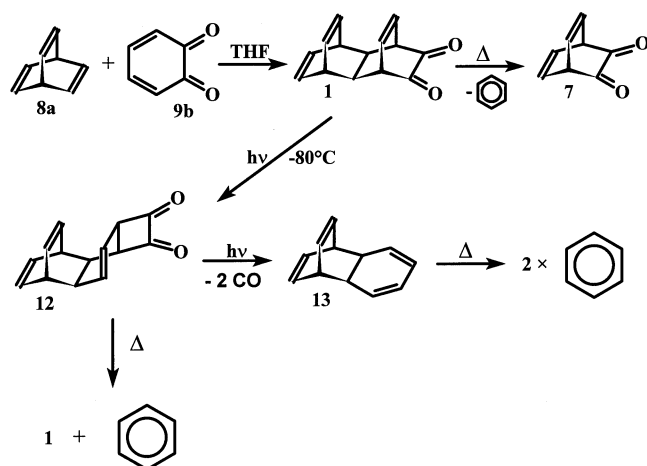
It is noteworthy that while ϕ_{-1} and ϕ_{12} were equal at room temperature, ϕ_{12} decreased much more rapidly than ϕ_{-1} as the temperature was reduced, and no reaction at all was observed at temperatures below about −90 °C. Examination of the NMR spectrum of the crude irradiation product of **1** at 0 °C indicated the presence of a small amount of **14** in the mixture. Temperature effects on the rearrangement to cyclobutanedione have been observed previously^[14] with a number of simpler enediones, although the formation of **14** is novel. This reaction could involve an intramolecular electron-transfer mechanism similar to that proposed for the reaction of isodrin analog **5** with nitriles. However, in the present case it is clearly a very inefficient process compared to the high chemical yield and quantum yield greater than unity observed with diene **5**^[5]. An alternative possibility for formation of **14** is the generation of a small amount of the triplet state of **1** in the direct irradiation. It is shown below that the sensitized reaction of **1** yields larger amounts of **14** demonstrating that the triplet state is the precursor of **14**.

Subsequent irradiation of cyclobutanedione **12** at 496 nm (or with a broad spectrum of light) in MCH at room temperature resulted in bisdecarbonylation and formation of benzene. The quantum yield at 496 nm was 0.24. Sensitized irradiation of **12** also produced benzene with a quantum yield close to unity. When the unsensitized reaction was performed at −80 °C, a new product, the *o,p'*-dibenzene **13** (1,4-etheno-1,4,4a,8a-tetrahydronaphthalene) was formed. This reaction and a detailed study of the subsequent retro Diels–Alder reaction of **13** to two molecules of benzene have been reported previously by us^[15].

The two additional diketones **10b** and **11** were also irradiated at 436 nm and both underwent singlet-state rearrangement to cyclobutanediones, characterized by their long-wavelength absorption in the visible, 485 nm for irradiation product of **10b** and 490 nm for the product from **11**. Here again, initial isosbestic behavior did not persist as irradiation was continued. Compound **10b** was very sensitive to moisture and its cyclobutanedione photolysis product was even more sensitive. In addition, the solubility of **10b** at the reduced reaction temperature required to observe

tetrabromo-*o,p'*-dibenzene was so low that further experiments in this direction were not undertaken. The octachloro compound **11**, on the other hand, did not suffer from such a problem. Details of its bisdecarbonylation and cycloreversion to tetrachloronaphthalene and tetrachlorobenzene are presented below.

Scheme 3

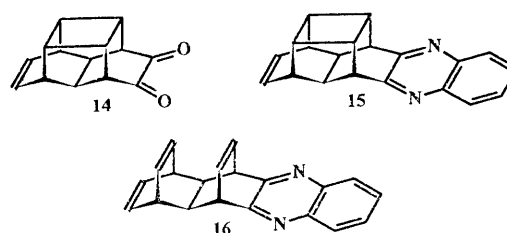


Sensitized Reaction

Irradiation of a mixture of **1** and benzophenone in de-oxygenated MCH or chloroform at 366 nm (all light absorbed by benzophenone) resulted in the disappearance of starting material with a quantum yield of 0.85, a value significantly larger than the quantum yield observed in direct irradiation. No new long wavelength absorption was observed; instead, weak new bands were observed at 453 (26), 460 (28), 470 (31), and 482 (30) nm. This type of fine structure is characteristic of the absorption spectra of saturated α -diketones. In contrast to the instability of **12**, the product of this sensitized reaction was a stable, yellow crystalline solid that could be isolated by column chromatography on silica gel. It was assigned the cage structure **14** on the basis of its spectroscopic properties, particularly the standard NMR analysis (see Experimental Section). Further support for the structure of **14** was provided by conversion with *o*-phenylenediamine to a quinoxaline **15**, which was identical with the product of sunlight irradiation of the quinoxaline **16**^[12]. In contrast to **1**, compound **14** exhibited strong phosphorescence with a maximum at 550 nm, a value characteristic of saturated α -diketones^[16]. Using CDCl_3 as solvent for sensitized irradiations the formation of **14** as well as benzene (by decarbonylation) could be monitored by NMR. No other by-products were observed.

At least two mechanisms can be considered for the triplet state reaction $\mathbf{1} \rightarrow \mathbf{14}$. Excitation to a low-lying triplet state of π, π^* character would lead to a mechanism in which the double bond of the cyclohexenedione chromophore reacts with the vicinal double bond in a typical cyclobutane-forming reaction. We note that the rigidity of **1** requires a [2 s

Scheme 4



+ 2 s] mechanism. Alternatively, the first step could be the formation of a biradical (see below) similar to the well-known oxadi- π -methane reaction^[9]. Bonding with the vicinal double bond could give a new biradical which collapses to **4**. We have suggested^[12] a similar azadi- π -methane type of initiation to explain the formation of cage quinoxaline **15** from the quinoxaline **16**.

Photolysis of Diketone **11**

As noted earlier, irradiation of **11** at 436 nm resulted in isomerization to an extremely sensitive cyclobutanedione, **17** [$\lambda_{\text{max}} = 490 \text{ nm}$ (120)]. Isolation or derivatization of **17** or **12** could therefore not be achieved. Here again, isosbestic points were observed (376, 465 nm) at early stages of the reaction but did not persist as the irradiation was continued. This is not surprising in view of the considerable overlap between absorption spectra of reactant and product, a characteristic also observed in the photolysis of **1**. However, in contrast to the behavior of **1**, there was very little temperature dependence^[18] in the isomerization of **11**; results at a number of temperatures are summarized in Table 3. Quantum yields decreased slightly with decreasing temperature but the isomerization to **17** remained the exclusive reaction (on the basis of UV/Vis data) over the entire temperature range from 220 to 298 K.

Table 3. Temperature dependence of quantum yields for reaction of $2 \cdot 10^{-3} \text{ M}$ of **11** in MCH/ CH_2Cl_2 (5:1, v/v) at 436 nm

T [K]	ϕ_{-11}	ϕ_{17}
298	0.17	0.15
258	0.15	0.14
243	0.12	0.13
235	0.12	0.10
220	0.09	0.07

It was therefore possible to irradiate **11** at reduced temperature using a broad spectrum of light ($\lambda > 380 \text{ nm}$) and obtain good conversion to the octachloro compound **18**. Results of such an experiment at -30°C are shown in Figure 2a.

The disappearance of **11** and isomerization to cyclobutanedione **17** can be observed in the long-wavelength region of the spectrum. Formation of the tetrachlorodiene chromophore **18** accounts for the new maxima appearing at 284, 293, 306, and 320 nm (Figure 2a) but isolation and further

Figure 2a. Spectroscopic changes between 260 nm and 340 nm upon irradiation of **11** (0.95 mg in 3 ml of MCH + 0.5 ml of CH₂Cl₂) at –30°C, $\lambda > 380$ nm

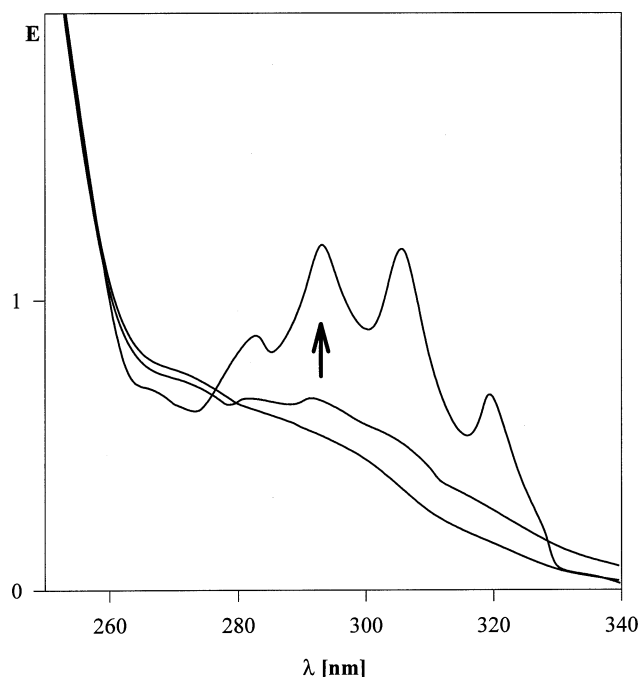
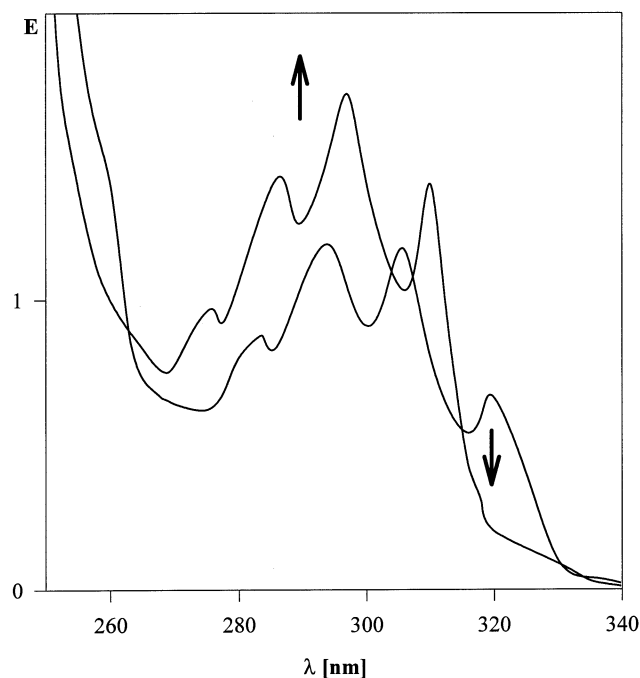


Figure 2b. Spectroscopic changes between 260 and 340 nm upon warming the photoproduct of **11** (Figure 2a) to 0°C



characterization of **18** could not be achieved. Warming the reaction mixture to room temperature and cooling back to –30°C gave rise to a new spectrum with maxima at 276, 287, 298, and 311 nm, extinction coefficients were on the order of 1000 (Figure 2b). These maxima are assigned to the mixture of 1,2,3,4-tetrachloronaphthalene and 1,2,3,4-tetrachlorobenzene, both of which result from the cycloreversion of **18**. These results combine to indicate a sequence of reactions similar to that reported previously by us^[15] for **1** involving rearrangement to a cyclobutanedione, bisdecarbonylation to a benzo-*o,p'*-dibenzene and retro Diels–Alder reaction to a naphthalene and a benzene.

A series of experiments was then performed in which solutions of **11** in MCH/dichloromethane (6:1)^[19] were irradiated at –30°C to generate **18** followed by rapid warming to a constant temperature around 0°C. Cycloreversion to 1,2,3,4-tetrachlorobenzene plus 1,2,3,4-tetrachloronaphthalene was then monitored by UV spectroscopy at 276, 287, and 298 nm. Good first-order behavior was observed. The first-order rate constants obtained in this way are summarized in Table 4.

We note that there is agreement among the values obtained at the three wavelengths. These results then lead to the following Arrhenius expression:

$$k = (4.4 \pm 0.8) \times 10^{11} e^{[-(18.8 \pm 1.2)/RT]}$$

The activation parameters (calculated for 298 K) are $\Delta H^\ddagger = 18.2 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -7.2 \text{ e.u.}$, and $\Delta G^\ddagger = 20.4 \text{ kcal mol}^{-1}$. Interestingly, these values are very close to the results reported by Grimme et al.^[20] for the corresponding unsubstituted compound, which undergoes thermal cyclo-

Scheme 5

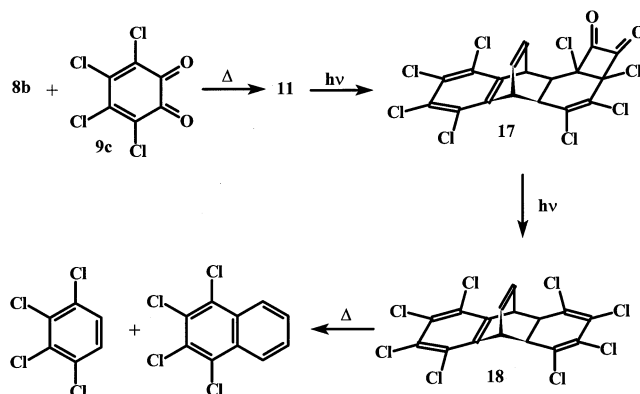


Table 4. First-order rate constants at three wavelengths for the thermal reaction of **18** at various temperatures

<i>T</i> [K]	$k_{276} \times 10^{-4} [\text{s}^{-1}]$	$k_{287} \times 10^{-4} [\text{s}^{-1}]$	$k_{298} \times 10^{-4} [\text{s}^{-1}]$
269.1	1.57	1.79	1.83
271.8	4.00	4.08	3.75
275.7	5.63	5.58	6.19
278.8	7.80	8.03	8.14
282.1	12.36	12.32	12.67

reversion to benzene and naphthalene. The eight chloro substituents have no significant effect upon the energetics of the retro Diels–Alder reaction.

Semiempirical AM1 Calculations

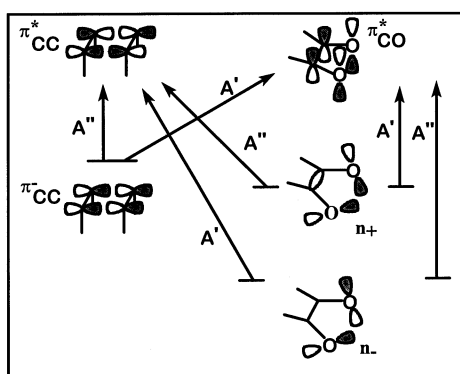
Semiempirical calculations were performed on compounds **1**, **12**, **14**, **15**, and **16** using the AM1 method^[17] including configuration interaction (50 singly and 25 doubly excited configurations). Ground states were calculated using symmetry-adapted geometry optimization. Geometry optimization of the first excited singlet state of **1** was also carried out. Results of these calculations are summarized in Table 5, which also includes calculated values for the absorption maxima. Only singlet states were considered because these calculations were in agreement with more sophisticated DFT calculations (see below). Triplet states were not treated with the AM1 method.

Table 5. Results of semiempirical AM1 calculations

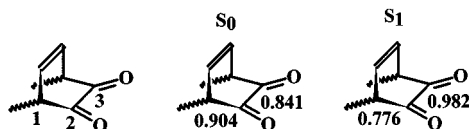
com- pound	state	symmetry of configuration	transition	$\lambda_{\text{calcd.}}$ [nm]	ΔE [eV]	λ_{exp} (lg ϵ) [nm]
1	S ₁	A'	$n+\pi^*_{\text{CO}}$	403	3.07	456 (2.161)
12	S ₁	A'	$n+\pi^*_{\text{CO}}$	388	3.19	496 (2.041)
14	S ₁	A'	$n+\pi^*_{\text{CO}}$	413	2.99	469 (1.491)
15	S ₁	A'	$\pi\pi^*$	314	3.94	316 (3.929)
16	S ₁	A	$\pi\pi^*$	311	3.98	318 (3.944)

The orbitals used for excited configurations are given in Figure 3.

Figure 3. Orbitals used for excited configurations

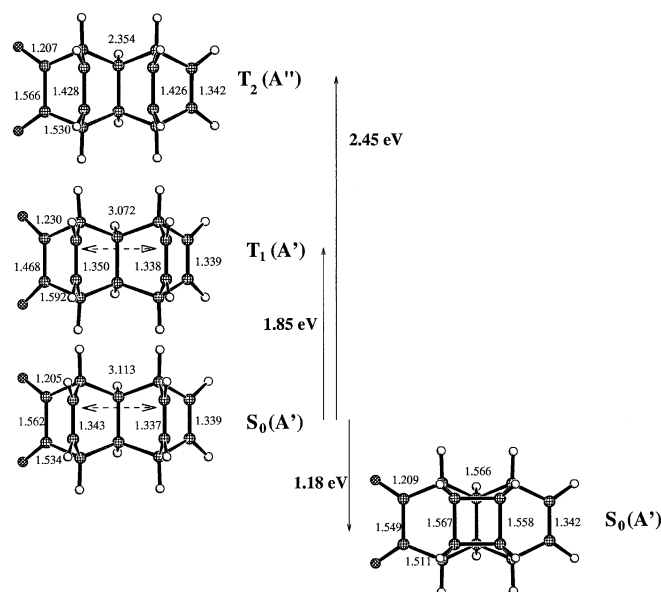


Excitation ($n+\pi^*$) of the carbonyl moiety is clearly required for the sigmatropic rearrangement of **1**. Comparing the change of the bond order of **1** on going from the ground state to the first excited state ($S_0 \rightarrow S_1$) as shown in Figure 4, an increase in the intercarbonyl bond order and a decrease in bond order between carbonyl groups and the adjacent non-ketonic carbon atoms are observed. This is the result that would be required for migration of an intact α -diketo grouping.

Figure 4. Bond-order changes during excitation of **1** (AM1)

Density Functional Calculations

Restricted and unrestricted density functional (DFT) calculations for the lowest singlet and triplet states of **1** have been performed with the TURBOMOLE suite of programs^[21]. We employed Beckes B3LYP hybrid exchange-correlation functional^[22] and AO basis sets of valence double-zeta quality augmented with polarization d-functions at the non-hydrogen atoms (VDZd)^[23]. Furthermore, the ground state of **14**, which is the formal reaction product of a $[2s + 2s]$ cycloaddition reaction, has been investigated. In order to obtain conclusive answers concerning the nature of the lowest excited states (which may be of $n\pi^*$ or $\pi\pi^*$ type) we have optimized the two lowest triplet states of **1** with $A''(\pi\pi^*)$ and $A'(\pi\pi^*)$ symmetry, respectively, at the unrestricted DFT level. The results for some structural and energetical data are summarized in Figure 5.

Figure 5. DFT-B3LYP/VDZd-optimized structures of several states of **1** and the S_0 state of **14**; the numbers refer to energy differences with respect to the S_0 state of **1**

The S_0 state of **1** has the expected structure with three localized C–C double bonds ($r_{\text{CC}} = 1.34 \text{ \AA}$) and a dione moiety with $r_{\text{CO}} = 1.205 \text{ \AA}$. The non-bonded distance (r_{NB}) between the carbon atoms of the double bonds closest to the carbonyl groups (depicted by the arrows in Figure 5) is 3.11 \AA , which is quite close to the sum of the van-der-Waals radii of carbon. The lowest triplet state (T_1) located 1.85 eV above the ground state is of A' symmetry and has $n\pi^*$ character. The structural changes occur exclusively in the two C–O double bonds in this state, i.e. the C–O distances increase to about 1.23 \AA while the C–C double bond moieties remain essentially unchanged compared to S_0 . From the T_1 ($n\pi^*$) of **1**, the reaction to the S_0 state of **14** is strongly exothermic by 3.03 eV (70 kcal/mol) and thus a low barrier is to be expected. However, this would involve a spin-forbidden singlet-triplet intersystem crossing so that the reaction probability may be too low.

The second triplet state of **1** has A'' symmetry and is of excited $\pi\pi^*$ character. It is located 2.45 eV above S_0 and 0.6

eV above the $T_1(n\pi^*)$. Structural changes occur in the moiety that is locally excited. This is seen by the increased C–C double-bond distance and a marked decrease in r_{NB} to 2.35 Å. Furthermore, we notice a pyramidalization of the carbon atoms of the C–C double bonds. Thus, in the $T_2(\pi\pi^*)$ state the possible product **14** with a cyclobutane fragment ($r_{NB} = 1.566$ Å, $r_{CC} = 1.57$ Å) is essentially preformed. The energetic difference of 0.6 eV between T_1 and T_2 is outside the normal error limits of DFT for such systems and properties, so we can safely assume that the lowest excited state of **1** is of $n\pi^*$ character. The relatively low excitation energy of the $T_1(\pi\pi^*)$ (2.45 eV) state e.g. compared to ethene (about 3.0 eV) seems to be a consequence of the bonding properties of the π^* orbital between the two double-bond fragments (see Figure 3).

Finally we want to discuss the vertical excited singlet and triplet states of **1**.

The results of DFT calculations including single excitations (DFT/SCI), a method developed to describe a wide range of excited states of organic molecules with relatively high accuracy^[24], are given in Table 6.

Inspection of the main configurations given in Table 6 reveals a quite complicated picture of the vertical excited state, which is in contrast to the findings from optimized geometries. With the exception of the lowest singlet and triplet state of A' symmetry, which are of pure $n\pi^*$ character, all states result from many primitive excitations that are strongly mixed with each other. Configurations made from charge-transfer excitations between the carbonyl and double-bond fragments are of relatively low energy.

Table 6. Vertical excitation energies (ΔE) and oscillator strengths (f) of some low-lying excited states of **1** at the DFT/SCI level; experimental values referring to band maxima in the UV spectrum are given in parentheses

state	ΔE [eV]	f	configuration
$2^1A'$	2.76 (2.7)	0.00156	$n\pi^*(32a' \rightarrow 33a')$
$1^1A''$	4.22 (4.3 ^[a])	0.00068	$n\pi^*(24a'' \rightarrow 33a') - n\pi^*(31a' \rightarrow 25a'')$
$3^1A'$	4.54 (4.6 ^[b])	0.01040	$\pi\pi^*(CT, 30a', 31a' \rightarrow 33a')$
$2^1A''$	4.68	0.00083	$n\pi^*(24a'' \rightarrow 33a') - n\pi^*(31a' \rightarrow 25a'')$
$3^1A''$	4.74	0.00001	$n\pi^*(CT, 32a' \rightarrow 25a'') + n\pi^*(24a'' \rightarrow 33a')$
$1^3A'$	2.35	—	$n\pi^*(32a' \rightarrow 33a')$
$1^3A''$	3.68	—	$n\pi^*(32a' \rightarrow 25a'') + \pi\pi^*(31a' \rightarrow 25a'')$
$2^3A''$	3.84	—	$\pi\pi^*(31a' \rightarrow 25a'') + n\pi^*(24a'' \rightarrow 33a')$

[a] Shoulder. — [b] Onset of strong absorption.

Photoelectron Spectrum of Diketone 7

It was not possible to record the photoelectron spectrum of diketone **1** due to its remarkable thermal lability. On the other hand, diketone **7**, a bicyclo[2.2.2]diketone very similar in number and arrangement of neighboring double bonds, was stable enough to give a satisfactory and instructive spectrum.

The assignments are given in Table 7 using the results of appropriate semiempirical calculations.

At first sight it might seem surprising and daring to assign a $\Delta n(n_- - n_+) = 3.0$ eV splitting to diketone **7** while

Figure 6. He(I) photoelectron spectrum of **7**

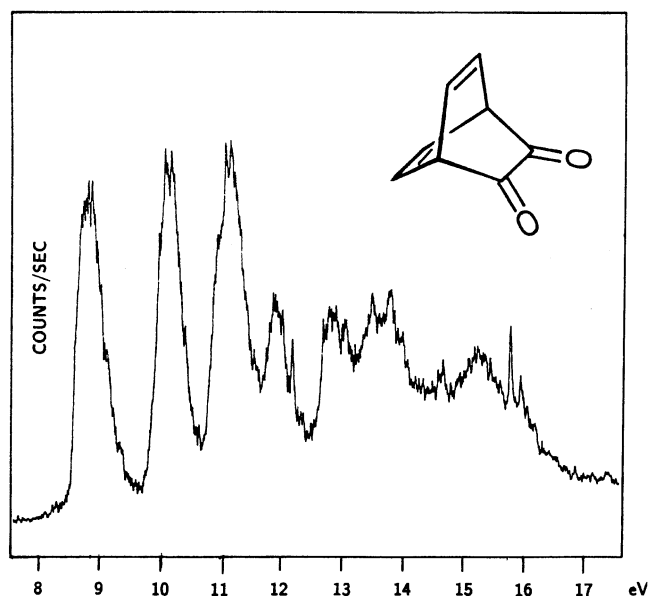
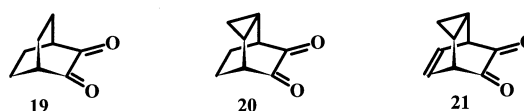


Table 7. Experimental and calculated ionization energies [eV] of **7**

I_{vj} (exp)	$-\epsilon$ (HAM/3)	$-\epsilon$ (MNDO)	$-\epsilon$ (MINDO/3)	assignment
8.80	9.06	9.80	8.67	$a_1(n_+)$
10.02	10.02	10.38	10.03	$b_1(\pi_-)$
11.11	10.85	11.40	10.57	$a_1(\pi_+)$
11.82	11.24	12.47	10.90	$b_2(n_-)$

the overwhelming number of α -diketones show $\Delta n(n_- - n_+) \approx 1.5 - 2.6$ eV^{[25][26]}. However, the interaction of the highest n_+ combination with lower lying appropriate π or cyclopropane Walsh orbitals can increase this $\Delta n(n_- - n_+)$ split considerably.

Scheme 6

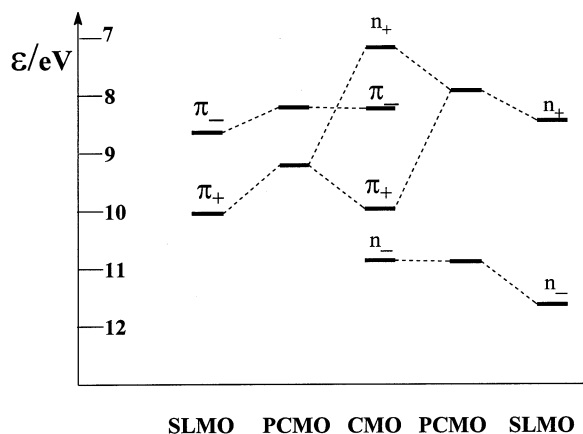


Gleiter et al.^[27] demonstrated that the moderate $\Delta n(n_- - n_+)$ value 1.5 eV in **19** is increased to significant values of 2.6 and 3.1 eV in **20** and **21**, respectively.

In order to verify these results at a higher and more plausible level, a procedure proposed by Heilbronner and Schmelzer^[28], based on the ab initio STO-3G model, was used. This method first creates localized bond orbitals (LBO) by application of the distance criterium of Foster and Boys^[29]. The Hartree-Fock matrix on the basis of LBOs is a non-diagonal one; the diagonal elements provide the basis energies of the LBOs. The off-diagonal matrix elements indicate the direct interaction parameters between the corresponding LBOs and thus give evidence of any through-space interaction. The LBOs are then transformed into new symmetry-adapted, semi-localized MOs. With

these as a new basis in the Hartree-Fock matrix, all non-diagonal elements in the rows and columns of the n orbital combinations or the π orbitals, respectively, were set to zero. Subsequent diagonalization yields precanonical energies and a transformation matrix. Application of this transformation matrix to the Hartree-Fock matrix in the basis of semi-localized MOs leads to the interaction matrix elements which link the precanonical MOs (PCMO) with the lone pairs or the π orbitals, respectively. This procedure was successfully applied to several cases of transannular interactions^{[30][31]}.

Figure 7. Ab initio STO-3G energies of semi-localized (SLMO), precanonical (PCMO) and canonical (CMO) molecular orbitals of **7** (see text)



The results for diketone **7** are given in Figure 7.

The most remarkable results of **7** are:

1. There is strong mixing of n_+ and π_+ PCMO combinations, which is the main cause for the enormous Δn ($n_- - n_+$) splitting. Calculated (3.6 eV) and experimental (3.0 eV) Δn ($n_- - n_+$) values are in good harmony.
2. In spite of the considerable $\pi\pi$ interactions (which lead to a final experimental splitting $\Delta\pi = \pi_- - \pi_+ = 1.1$ eV) the highest MO is not, as could have been expected, the π_- combination but still the n_+ orbital.

We can assume that diketone **7**, with its two laticyclic homoconjugated double bonds, represents a good model for the interactions in **1**. It is accordingly logical to conclude that in **1**, too, the n_+ combination constitutes the HOMO. The consequences for **1** are important and are confirmed by the DFT calculations: Lowest excited states in the singlet as well as the triplet manifolds are of $n\pi^*$ type, and the $\pi\pi^*$ singlet transition appears only third at about 4.6 eV (270 nm).

Conclusions

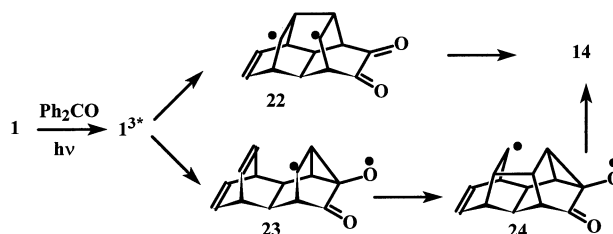
The diverse photoreactions of **1** may be discussed in terms of several reasonable mechanisms. The reactivity of excited $^1n_+\pi^*$ state is clearly indicated by the bond order changes (Figure 4) as well as the bond length changes (Figure 5). No intramolecular cycloaddition is expected to take

place in this state, rather α -cleavage and sigmatropic rearrangement, as are observed, are predicted.

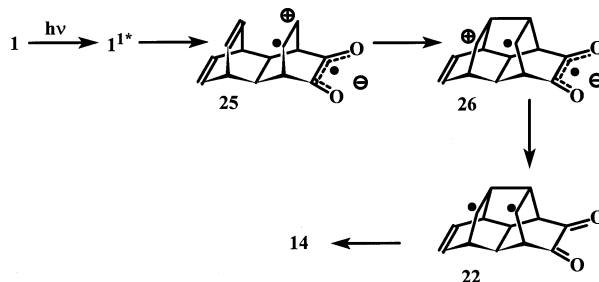
The forecast for the lowest triplet state $^3n\pi^*$ is similar. As described above the calculational evidence predicts that the intramolecular $[2\pi + 2\pi]$ photocycloaddition starts from this triplet state. An intramolecular SET mechanism via **25**, **26** and **22**, as shown in Scheme 7, could also conceivably occur, at least in polar solvents, since the ionization energy of the homoconjugated triene subchromophore in **1** should be very similar to that of diene **5** (8.08 eV^[5]). As discussed in the introduction an SET mechanism has been observed for **5** and 2-cyanonaphthalene^[5]. The analogous intramolecular SET process in **1** can therefore be discussed as a plausible alternative in polar solvents. We are inclined to conclude that, among the proposals shown in Scheme 7, the pathway via diradical **23** (on account of the low-lying $^3n\pi^*$ state) but not **22** is a very likely one for the sensitized photolysis of **1** in non-polar solvents.

Scheme 7

A. Triplet Mechanisms



B. SET Mechanism



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Experimental Section

General: Melting points: SMD-20 Büchi apparatus, values uncorrected. – Preparative thin layer chromatography: Merck Art. 7749 silica gel 60 PF₂₅₄ (70–230 mesh). – NMR: Tetramethylsilane was used as the internal standard; ¹H NMR: Varian VXR 300, Bruker WP 80, and Bruker WM 400 instruments; ¹³C NMR: Varian VXR 300 at 75 MHz. – IR: Perkin Elmer 710 B. – MS:

MAT 312 Finnigan and MAT 711 Varian instruments (both 70 eV). – UV/Vis: Cary Model 15 and 2200 instruments. – PES: Leybold-Heraeus UPG 200. – Elemental analyses: Institute of Pharmaceutical Chemistry of the University of Düsseldorf. – Photochemistry: an Osram 200-W high-pressure mercury lamp in a Wild housing was used for small-scale preparative irradiations as well as a Canard-Hanovia 900-W Hg-Xe lamp in a Schoeffel housing for some preparative runs. Quantum yields were determined at room temperature using the colored form of Aberchrom 540 as the actinometer^[32] and the decrease in the long-wavelength diketone absorption for the calculation of concentration changes. The light source used was a Phillips 125-W medium-pressure mercury lamp. The 436-nm mercury line was isolated with a Schott interference filter.

Tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-9,11,13-triene-4,5-dione (1): Freshly prepared *o*-benzoquinone (800 mg, 7.2 mmol) was added with stirring to a solution of 1.28 g (12.3 mmol) of barrelene (prepared according to ref.^[33]) in 4 ml of THF in a 50-ml round-bottomed flask. Addition of the same quantity of *o*-benzoquinone to the continuously stirred solution was repeated on a daily basis for 10 d. Insoluble decomposition products of benzoquinone were removed by filtration and the remaining product was purified by chromatography using a 30-cm column packed with 40 g of Merck silica gel 60. Concentration and crystallization from CH₂Cl₂/diethyl ether (1:2) gave 400 mg of **1** (15%) as orange-colored prisms, m.p. 126–129°C. The compound was stored at 0°C in the dark. – IR (KBr): $\tilde{\nu}$ = 3050 cm⁻¹, 2970, 2910, 1740 sh, 1730 (C=O), 1355, 1230, 765, 720. – UV/Vis (MCH): λ_{\max} (lg ϵ) = 456 nm (2.16). – ¹H NMR (CDCl₃): δ = 2.45 (s, 2 H), 3.43 (t, 2 H), 3.61 (m, 2 H), 5.93 (t, 2 H), 6.14 (t, 2 H), 6.57 (t, 2 H). – MS: Only the fragments **7** and benzene could be detected. – C₁₄H₁₂O₂ (212.3): calcd. C 79.22, H 5.70; found C 78.69, H 6.26. Correct elemental analyses were obtained using the quinoxaline derivative **16**: C₂₀H₁₆N₂ (284.4): calcd. C 84.48, H 5.67, N 9.85; found C 84.55, H 5.70, N 9.80.

Thermolysis of 1. – *Bicyclo[2.2.2]octa-5,7-diene-2,3-dione (7)*: The adduct **1** (120 mg, 0.57 mmol) was heated for 4 min, in a flask fitted with an air condenser, at a bath temperature of 140°C, and the yellow sublimate was collected. The product **7** (73 mg, 96%) was purified by sublimation (21 mbar, bath temp. 70°C), m.p. 107–108°C (ref.^[10]; m.p. 107–108°C). Further evidence for the identity of this compound was obtained from its spectroscopic properties.

Sensitized Irradiation of 1. – *Hexacyclo[6.4.2.0^{2,7}.0^{3,11}.0^{6,10}.0^{9,12}]tetradec-13-ene-4,5-dione (14)*: Freshly recrystallized **1** (64 mg, 0.302 mmol) and benzophenone (198 mg) were dissolved in CDCl₃ (30 ml) in a quartz cell of 4 cm light path and the solution degassed by bubbling dry argon through it for 30 min. The cell was sealed off and irradiated with light from the 900-W Xe-Hg high-pressure lamp through a combination of a Schott 366-nm interference filter and a Schott heat filter (KG1). Using NMR spectroscopy, the formation of **14** as well as that of benzene (by decarbonylation) could be monitored. After 2 h, the yellow-orange color had almost completely disappeared. The solvent was removed in vacuo and the semicrystalline residue was chromatographed on 4.6 g of silica gel using CH₂Cl₂ as eluent. The light yellow fraction was collected and concentrated to give long yellow needles of **14** (16 mg, 25%), m.p. 224–227°C. – IR (KBr): $\tilde{\nu}$ = 3040 cm⁻¹ (=CH), 2980, 2960, 2930 (–CH), 1745, 1720 (C=O), 1250, 1215, 1030, 800, 720, 705 sh, 695. – UV/Vis (CH₂Cl₂:cyclohexane 1:9): λ_{\max} (ϵ) = 453 nm (26), 460 (28), 470 (31), 482 (30). – Emission spectrum (MCH/isopentane/CH₂Cl₂, 77 K, λ_{exc} = 450 nm): λ_{em} = 550 nm. – ¹H NMR

(CDCl₃): δ = 2.34 (br. s, 2 H, 2-H, 7-H), 2.61 (br. s, 2 H, 9-H, 12-H), 2.74 (br. s, 2 H, 3-H, 6-H), 2.80 (br. s, 2 H, 1-H, 8-H), 3.19 (br. s, 2 H, 10-H, 11-H), 6.34 (dd, 2 H, 13-H, 14-H). – ¹³C NMR (CDCl₃): δ = 37.9 (C-10, C-11), 40.7 (C-1, C-8), 41.3 (C-9, C-12), 41.6 (C-2, C-7), 52.1 (C-3, C-6), 130.1 (C-13, C-14), 197.3 (C-4, C-5). – MS (70 eV); m/z (%): 213 (100) [M⁺], 205 (100), 206 (87) [M⁺ – C₆H₆]. – C₁₄H₁₂O₂ (212.3): calcd. C 79.22, H 5.70; found C 78.90, H 5.90. Quinoxaline derivative **15** gives correct elemental analysis: see below.

3,6,13,14-Tetrabromotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-9,11,13-triene-4,5-dione (10b): A solution of 95 mg of barrelene in 3 ml of dry THF was stirred with tetrabromo-*o*-quinone (**9a**, 390 mg, 920 μ mol) at room temp. for 8 h. After the addition of 1 ml of dry ether, colorless needles (45 mg, 9%) of 4,5-tetrabromobenzo-3,6-dioxatricyclo[6.2.2.0^{2,7}]dodeca-4,9,11-triene (**10a**) crystallized and were removed by filtration, m.p. 206°C. The orange filtrate was concentrated and the semi-solid oil, containing partially crystallized material, was dissolved in 2 ml of CH₂Cl₂/ether (1:1). The solution was allowed to stand at –20°C for 10 h and small orange prisms of **10b** (160 mg, 33%) were isolated, m.p. 150°C. The compound was very moisture-sensitive and was stored in the dark at a temperature below 0°C. – UV/Vis (CH₂Cl₂:cyclohexane 1:3): λ_{\max} (lg ϵ) = 440 nm (1.81). – ¹H NMR (CDCl₃): δ = 2.65 (br. s, 2 H, 2-H, 7-H), 4.28 (m, 2 H, 1-H, 8-H), 6.37 (m, 2 H, 9-H, 10-H), 6.53 (m, 2 H, 11-H, 12-H). – Quinoxaline derivative of **10b**: C₂₀H₁₂Br₄N₂ (599.9): calcd. C 40.04, H 2.01; found C 40.12, H 2.10. – Data of **10a**: ¹H NMR (CDCl₃): δ = 4.23 (mc, 2 H, 1-H, 8-H), 4.43 (br. s, 2 H, 2-H, 7-H), 6.30 (m, 4 H, olefinic). – C₁₄H₈Br₄O₂ (527.8): calcd. C 31.86, H 1.53; found C 31.90, H 1.55.

3,4,5,6,10,11,12,13-Octachloropentacyclo[6.6.2.2^{3,6}.0^{2,7}.0^{9,14}]octadeca-4,9,11,13,15-pentaene-17,18-dione (11): A mixture of tetrachlorobenzobarrelene (2.06 g, 7.06 mmol)^[15b] and tetrachloro-*o*-benzoquinone (1.7 g, 6.91 mmol) was heated in dry toluene (5 ml) at 80–95°C under nitrogen with stirring in the dark for 5 h. After 2 h, the color of the dark red solution became lighter. The reaction mixture was filtered under nitrogen and the isolated yellow crystals were washed with dry pentane (8 ml) and then with anhydrous ether. Drying in a nitrogen stream yielded yellow crystals (2.42 g, 65%), m.p. 235–240°C. – IR (KBr): $\tilde{\nu}$ = 3080 cm⁻¹, 3060, 3030, 2990, 1760, 1740, 1590, 1470, 1370. – UV/Vis [MCH/CH₂Cl₂ (5:1)]: λ_{\max} (lg ϵ) = 448 nm (2.14). – ¹H NMR (CDCl₃): δ = 2.60 (br. s, 2 H, 2-H, 7-H), 5.00 (mc, 2 H, 1-H, 8-H), 6.55 (m, 2 H, 11-H, 12-H). – Quinoxaline of **11**: C₂₄H₁₀Cl₈N₂ (609.9): calcd. C 47.26, H 1.65, N 4.59; found C 47.35, H 1.61, N 4.63.

3,10-Diaza-Octacyclo[11.8.1.0^{2,11}.0^{4,9}.0^{12,20}.0^{14,19}.0^{15,22}.0^{16,21}]docosa-2,4,6,8,10,17-hexaene (15): A mixture of **14** (1.1 mg, 5.2 μ mol) and *o*-phenylenediamine (5 mg, 46 μ mol) in CH₂Cl₂ (3 ml) decolorized rapidly at room temp. After 30 min, the solvent was evaporated at 80°C and the residue triturated with 1 ml of ether. Sublimation in vacuo gave colorless crystals of **15** (0.7 mg, 48%) with a m.p. of 226–230°C. This melting point was not depressed on admixture with an authentic sample of **15**^[12], and the IR spectra were identical.

☆ Dedicated to Professor *Dietrich Mootz* on the occasion of his 65th birthday.

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