Electron Donor-Acceptor Compounds, 50[1]

Oligooxa[3*n*.3]paracyclophane Quinhydrones – Cation-Induced Charge-Transfer Absorptions and Structures of the Metal Complexes

Helmut Bauer*, Volker Matz, Martina Lang, Claus Krieger, and Heinz A. Staab

Abteilung Organische Chemie, Max-Planck-Institut für medizinische Forschung, Jahnstraße 29, D-69120 Heidelberg, Germany

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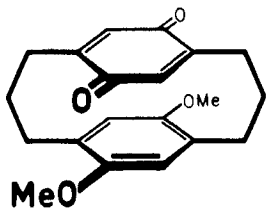
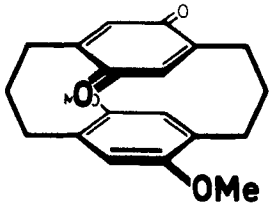
The intramolecular oligooxa[3*n*.3]paracyclophane quinhydrones **2**–**5** (with $n = 3$ to 6) were synthesized and their interactions with alkali and alkaline earth metal and mercury(II) ions were studied by electron absorption and NMR spectroscopy. Remarkable enhancements of the CT absorptions were observed by complexation with metal ions of the pentaoxa[15.3]paracyclophane quinhydrone **4** and the hexaoxa[18.3]paracyclophane quinhydrone **5** to the corresponding complexes **6a**–**e** and **7**, respectively. The various donor-acceptor orientations and the crown ether-like complexation in the calcium complex **6d**, the mercury complex **6e** and the barium complex **7** were determined by X-ray analysis. Moreover, the X-ray structures of the tetramethoxy-2,5,8-trioxa[9.3]paracyclophane **8a**, a precursor of the quinhydrone **2**, and of the pentaoxa[15.3](2,5)-*p*-benzoquinonophane **20**, the product of oxidative demethylation of the quinhydrone **4**, are given. For comparison with the cyclic quinhydrones acyclic analogs are also described.

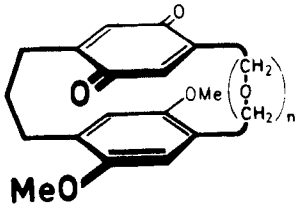
In previous papers quinhydrones of [2.2]- to [6.6]paracyclophanes and their dimethyl ethers[2a–c] containing two equal oligomethylene bridges were studied with regard to the dependence of their charge-transfer (CT) absorption on distance, mutual orientation, and the degree of the fixation of the donor and acceptor components. In this series the [3.3]paracyclophane quinhydrone dimethyl ether **1a** in the pseudogeminal structure showed the most intense CT absorption band ($\lambda_{CT} = 475$ nm, $\varepsilon = 3000$)[2b], because the donor and acceptor components obviously are optimally arranged for an intramolecular interaction. The CT absorption of the pseudoortho isomer **1b** ($\lambda_{CT} = 500$ nm, shoulder, $\varepsilon = 100$ and 367 nm, $\varepsilon = 1740$)[2b] was considerably less distinct.



1a



1b



2: n = 3
3: n = 4
4: n = 5
5: n = 6

Results and Discussion

As a variation of these carbon-bridged donor-acceptor [3.3]cyclophanes we synthesized the compounds **2**–**5**[3], in which one of the trimethylene bridges of **1a**/**1b** is modified by a polyether chain consisting of (CH_2OCH_2) units of varying length. We expected distinct CT absorptions for the lower homologs **2** and **3**, because due to the relative short polyether bridges – although less fixed than in **1a** and **1b** – the donor-acceptor components should approach each other relatively closely. For the higher homologs **4** and **5**, however, only weak CT effects were expected due to the width and flexibility of the larger macrocyclic ring. However, just for these larger quinhydrones an approach and a fixation of the donor and acceptor should be achieved by means of complexation of the crown ether-like bridges with suitable alkali or alkaline earth metal ions. Thereby, an enhancement of the CT absorption compared to the corresponding uncomplexed compounds should result. The bonding between alkali and alkaline earth metal ions and crown ethers[4a] depends mainly on the relation between the diameter of the cations and the cavity size, on the number of the donor atoms, and the solvent. Na^+ and Ca^{2+} ions and K^+ and Ba^{2+} ions, resp., were therefore considered for

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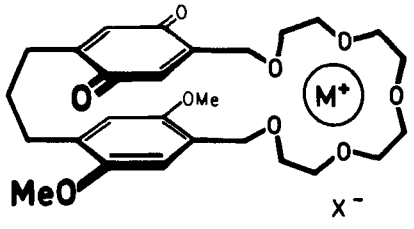
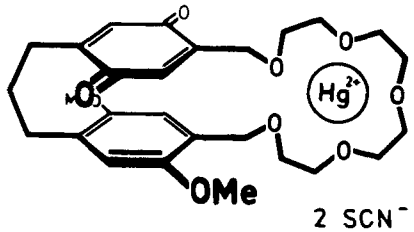
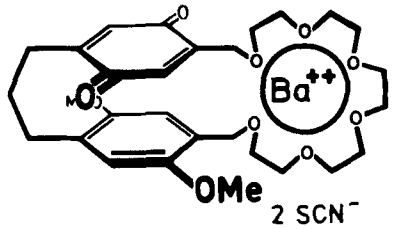
the complexation of the quinhydrones **4** and **5**. A significant conformational modification of a bisparaphenylene crown ether containing an OCH_2O and an $O(CH_2CH_2O)_4$ bridge by complexation with sodium ions has recently been described[4b]. Since mercury(II) complexes[5a,b] with $(CH_2OCH_2)_5$ ligand systems are also known, we used mercury(II) ions for the complexation of compound **4**, too. Indeed, the sodium complexes **6a–c**, the calcium complex **6d**, the mercury complex **6e**, and the barium complex **7** were obtained in crystalline form. They are the first examples of cation-selective complex ligands with a "built-in" CT indicator[3].



6a: $M^+ = Na^+$, $X^- = SCN^-$
6b: $M^+ = Na^+$, $X^- = I^-$
6c: $M^+ = Na^+$, $X^- = ClO_4^-$
6d: $M^+ = Ca^{2+}$, $X^- = 2\ SCN^-$



6e



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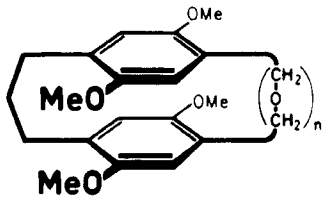
The approach of the donor and acceptor components in the complexes could be detected by electron absorption and NMR spectroscopy. For the spectroscopic studies of the quinhydrone complexes chloroform was used as solvent, because it dissolves the complexes, but not the free cations. For a quick detection of an interaction of the metal ions with the paracyclophane quinhydrones **2–5** as well as their corresponding tetramethoxyparacyclophane precursors **8–11** solutions of these compounds in chloroform were shaken with solid alkali, alkaline earth, or mercury(II) thiocyanate for 5 minutes. During this process the metal thiocyanates, although nearly insoluble in chloroform, dissolved readily by forming the complexes in analogy to the known conversion of crown ethers with alkali and alkaline earth salts. By this method only as much metal salt is dissolved as is required for the complexation not disturbing the CT absorptions in the electron spectrum and the signal shifts of the complexes in the NMR spectrum by high salt concentrations. Decomplexations were achieved by adding stronger ligands to the metal complex solutions and were detected by electron and NMR spectroscopy. Whereas in the [15.3]- and [18.3]paracyclophane quinhydrones **4** and **5** the donor and the acceptor components can rotate freely, their orientations in the corresponding complexes **6** and **7** were expected to be fixed as in pseudogeminal **1a** or the pseudoortho isomer **1b**. Similar structures were also assumed for the smaller [9.3]paracyclophane quinhydrone **2** and the tetramethoxy[9.3]paracyclophane **8** due to the relatively short polyether bridges. The X-ray structure analysis revealed that the donor and acceptor orientation in the crystallized calcium complex **6d** is pseudogeminal, in the mercury complex **6e** and the barium complex **7**, however, pseudoortho with horizontally shifted donor and acceptor moieties.

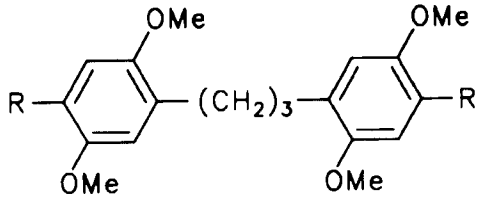
Syntheses

The synthesis of the paracyclophane quinhydrones **2–5** started from the corresponding tetramethoxyoligooxaparacyclophanes **8–11**.

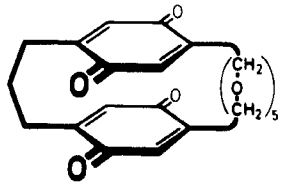
11,14,20,23-Tetramethoxy-2,5,8-trioxa[9.3]paracyclophane (**8**) was obtained by the condensation of 1,3-bis[4-(hydroxymethyl)-2,5-dimethoxyphenyl]propane (**15**) with diethylene glycol ditosylate[6] as well as by the conversion of 1,3-bis[4-(bromomethyl)-2,5-dimethoxyphenyl]propane (**16**) with diethylene glycol under high-dilution condition. The tetramethoxycyclophanes **9–11** were synthesized analogously from the cyclization components **13** and **16** and the corresponding oligoethylene glycols. Compounds **13** and **16** were prepared by chloro- and bromomethylation, resp., of 1,3-bis(2,5-dimethoxyphenyl)propane (**12**)[7], which is easily accessible by condensation of 2,5-dimethoxybenzaldehyde with 2,5-dimethoxyacetophenone via the α,β-unsaturated ketone 1,3-bis(2,5-dimethoxyphenyl)-2-propene-1-one and its stepwise catalytic hydrogenation. The two-step hydrogenation of the α,β-unsaturated ketone is superior to the hydrogenation in one step, as the yield and the degree of purity of **12** in the latter case are considerably lower. The diol **15** was easily prepared by conversion of the bis(chloromethyl) compound **13** into the diacetate **14** and hydrolysis of the latter with sodium hydroxide[8]. The partial oxidative demethylation of the tetramethoxycyclophanes **8–11** with ammonium hexanitratocerate led to the crystalline oligooxa[3*n*.3]paracyclophane quinhydrone dimethyl ethers **2–5**, the colors of which range with increasing length of the polyether bridge from red-orange to yellow. The sodium complexes **6a–c**, the calcium complex **6d** and the mercury complex **6e** were obtained as red crystals by conversion of the orange [15.3]paracyclophane quinhydrone **4** with NaSCN, NaI, $NaClO_4$,



8: n = 3
9: n = 4
10: n = 5
11: n = 6



12: R = H
13: R = CH_2Cl
14: R = CH_2OAc
15: R = CH_2OH
16: R = CH_2Br
17: R = CH_3
18: R = CH_2OMe
19: R = CH_2OEt



20

$Ca(SCN)_2 \cdot 4\ H_2O$, and $Hg(SCN)_2$, resp. The barium complex **7** was produced by heating of the yellow [18.3]paracyclophane quinhydrone **5** and $Ba(SCN)_2 \cdot 2\ H_2O$ with triethyl orthoformate in acetone or acetonitrile in order to eliminate water. Oxidative demethylation of the tetramethoxycyclophane **10** or of the quinhydrone **4** with diammonium hexanitratocerate in the presence of 2,6-pyridinedicarboxylic acid *N*-oxide[9] gave the pentaoxa-[15.3](2,5)-*p*-benzochinonophane **20**.

Electron Spectra

The spectra of the trioxa[9.3]- and the tetraoxa[12.3]paracyclophane quinhydrones **2** and **3**, resp., in chloroform are nearly identical. They show a distinct CT absorption band, which is, however – compared to the [3.3]paracyclophane quinhydrone dimethyl ether **1a** – considerably weaker and hypsochromically shifted because of the 9- and 12-membered polyether chain, resp.

Addition of solid NaSCN or KSCN and shaking of the chloroform solution for 5 minutes did not change the absorption band of the [9.3]paracyclophane quinhydrone **2**, whereas for the [12.3]paracyclophane quinhydrone **3** a very slight change of the absorption band was observed. The number of the ether oxygen atoms in the bridges of **2** and **3** is obviously not sufficient for a suitable coordination of sodium or potassium ions. In the case of **3**, however, the oxygen atom of a methoxy group could be used in addition to the four ether oxygen atoms in the bridge. But according to CPK models this configuration cannot achieve a favorable CT arrangement of donor and acceptor. This might explain the decreasing intensity of the CT absorption.

Table 1. CT absorptions of the oligooxa[3*n*.3]paracyclophane quinhydrones **2**–**5** in $CHCl_3$ and their changes caused by cations

Added salt	λ_{CT} nm (ε) of 2	3	4		5
–	467 (540)	467 (495)	462 (324)		442 (213)
NaSCN[a]	467 (540)	464 (462)	478 (874)		459 (375)
NaSCN			480 (996)	**6a**	
NaI			479 (959)	**6b**	
$NaClO_4$			478 (918)	**6c**	
$Ca(SCN)_2$			478 (1207)	**6d**	
KSCN[a]	467 (540)	465 (482)	464 (374)		465 (352)
$Hg(SCN)_2$			475 (864)	**6e**	
$Ba(SCN)_2$[a]			438 (508)		470 (562)
$Ba(SCN)_2$					472 (597) **7**

[a] With shaking of the chloroform solution with the corresponding salt.

Compared to the trioxa[9.3]paracyclophane quinhydrone **2** the CT absorption band of the pentaoxa[15.3]paracyclophane quinhydrone **4** differs only slightly in its position, largely, however, in its intensity. After shaking of a chloroform solution of **4** with solid NaSCN for 5 minutes the intensity of the CT band rose dramatically with a simultaneous bathochromic shift of the absorption maximum (Table 1, Figure 1). This change, which can be easily detected visually, is reversible by adding the stronger chelating agent 4,7,13,16,21-pentoxa-1,10-diazabicyclo[8.8.5]tricosane (Cryptofix 221) or 18-crown-6. The sodium complex **6a** (λ_{CT} = 480 nm, ε = 996, concentration 10^{-3} mol/l) prepared in crystalline form shows in chloroform – apart from a slightly higher intensity – the same spectrum as the chloroform solution of **4** after treatment with solid NaSCN (Figure 1). As the extinction coefficient remains almost constant on dilution of the chloroform solution of **6a** from 10^{-3} to 10^{-4} mol/l,intermolecular interactions can be excluded for the formation of the CT absorption band. Furthermore, it can be assumed that the sodium complex **6a** in chloroform is stable and hardly dissociated. If, however, a drop of methanol is added to the chloroform solution of the complex an immediate dissociation with fading out of the color is observed. The CT absorption of the sodium complexes **6a**–**c** is nearly independent of the kind of the anion (Table 1).

By shaking of the chloroform solution of the pentaoxa-[15.3]paracyclophane quinhydrone **4** with KSCN the enhancement of the CT absorption becomes considerably weaker, and the band is hardly shifted. This might be due to the bigger potassium ion (2.66 Å diameter), which is not as suitable for the coordination with the $(CH_2OCH_2)_5$ unit of **4** as the sodium ion (1.94 Å diameter).

With $Ba(SCN)_2$ the intensity of the CT absorption of the quinhydrone **4** is increased stronger than with KSCN, but

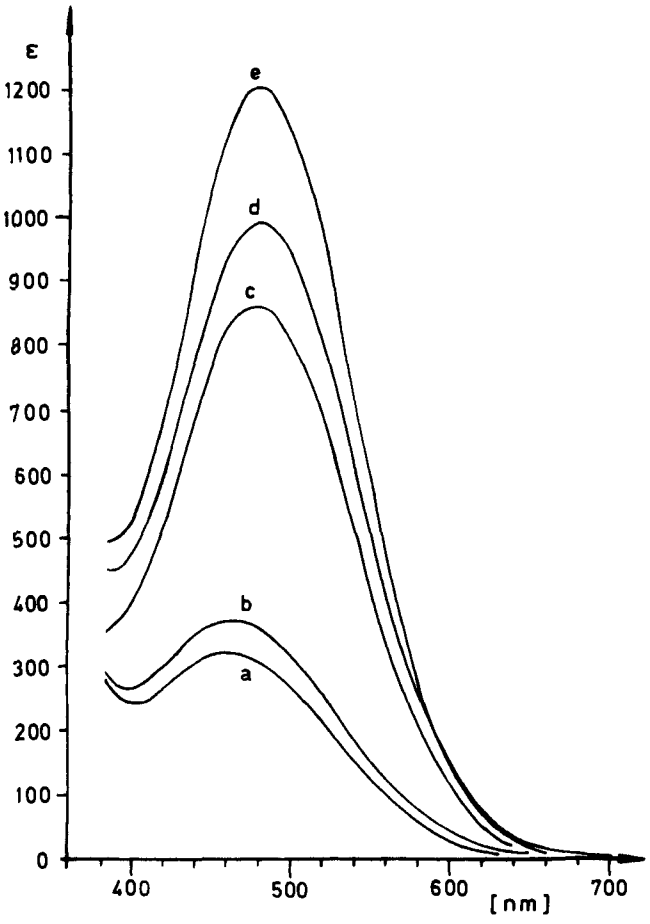


Figure 1. CT absorption in $CHCl_3$. – a) **4**, b) after shaking of **4** with KSCN for 5 min, c) **6e**; after shaking of **4** with NaSCN for 5 min, d) **6a**, e) **6d**

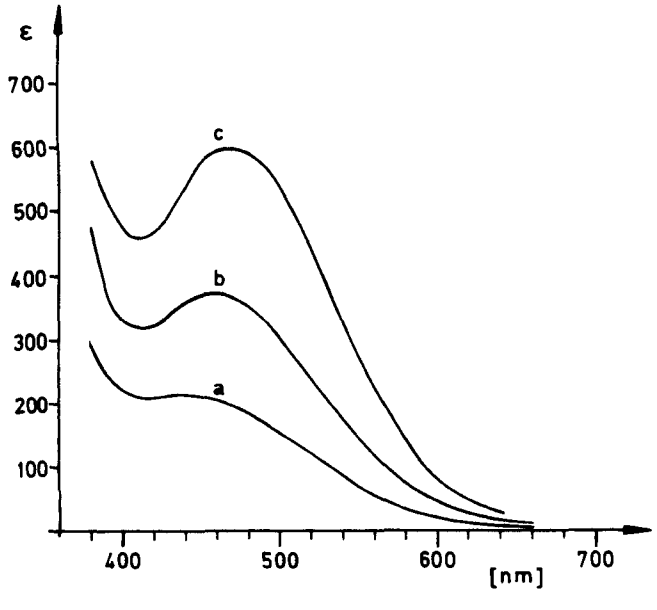


Figure 2. CT absorption in $CHCl_3$. – a) **5**, b) after shaking of **5** with NaSCN for 5 min, c) **7**

the CT maximum is hypsochromically shifted. The barium ion, whose diameter (2.68 Å) is very close to that of the potassium ion, may owing to its double charge and its tendency towards a higher coordination number attract in addition to the 5-bridging ether oxygens a further oxygen atom of a methoxy group for the coordination leading to an orientation of the donor and acceptor unfavorable for a charge transfer.

The position of the CT band of the quinhydrone-calcium thiocyanate complex **6d** is almost identical with that of the sodium complexes **6a–c**. Its intensity, however, is much stronger (Figure 1). This enhancement may be explained by the fact that the calcium ion (1.98 Å diameter) has approximately the same size as the sodium ion, yet due to its double charge it is able to form a stronger coordinative bond with the bridging ether oxygens and may thus achieve a closer approach of the donor and acceptor than the sodium ions in the complexes **6a–c**.

The CT absorption of the quinhydrone-mercury(II) dithiocyanate complex **6e** is similar to that of the sodium complex **6a**, although the intensity is somewhat lower. This might be attributed to the fact that the diameter of the mercury ion (2.20 Å) is larger than that of the sodium or calcium ion and that, owing to the relatively large homoplanar bond between Hg^{2+} and SCN^-, the double charge cannot become as effective in the coordination of the bridging ether oxygens as in the case of the calcium ion. Consequently, the donor and the acceptor could not approach as closely on the side of the polyether loop as in the sodium complexes **6a–c** or in the calcium complex **6d**.

Furthermore, Hg^{2+} is, according to the "HSAB theory", classified as a soft metal ion in contrast to Na^+ and Ca^{2+} and therefore its interaction with the "hard" oxygen ligands is weaker.

Compared to the smaller quinhydrone homologs **2–4** the intensity of the CT band of the largest hexaoxa[18.3]paracyclophane quinhydrone **5** is even weaker because of the longer polyether bridge conditioning a greater flexibility. The CT band is exhibited merely as a flat maximum which is hypsochromically shifted compared to that of **4** (Table 1 and Figure 2). The effect of sodium ions on the largest quinhydrone **5** is significant, however considerably weaker than with **4**. Conversely, the potassium ions produce a stronger effect with **5** than with **4**, as the bigger potassium ion may be better coordinated by the 6 oxygens of the longer polyether loop. A coordination by six ether oxygens is also favored by the barium ion. So by the addition of solid $Ba(SCN)_2 \cdot 2\ H_2O$ to a chloroform solution of the quinhydrone cyclophane **5** and shaking of the mixture for 5 minutes a clearly discernible maximum is revealed by an intensity enhancement of the CT absorption. A solution of the isolated barium complex **7** shows almost the same CT absorption (λ_{CT} = 472 nm, ε = 597) (Figure 2). Position and intensity of this CT band prove that on the complexation of the [18.3]paracyclophane quinhydrone **5** with barium ions the donor and acceptor moieties approached each other as was found in the sodium complexes **6a–c**, the calcium complex **6d** and the mercury complex **6e** of the [15.3]paracyclophane quinhydrone.

NMR Spectra

The signals of the two aromatic hydrogen atoms of the smallest quinhydrone **2** recorded in $CDCl_3$ are shifted downfield in comparison with those of the benzoquinone hydrogens. The same signal pattern applies to the higher homolog **3**. In the spectrum of **2**, however, it is remarkable that the benzylic CH_2 hydrogen atoms at the aromatic ring and the allylic CH_2 hydrogens at the benzoquinone ring both appear as AB systems. This is due to the limited free rotation of the CH_2 groups at the ends of the relatively short polyether bridge. Both AB systems remain constant even up to 387 K in $[D_6]$DMSO.

Table 2. ^{1}H-NMR signals of the oligooxa[3*n*.3]paracyclophane quinhydrones **2**–**5** in $CDCl_3$ and their shifts caused by cations

Comp.	Aromat. H ortho to $(CH_2OCH_2)_n$	Aromat. H ortho to $(CH_2)_3$	Quinone H vic to $(CH_2OCH_2)_n$	Quinone H vic to $(CH_2)_3$	Benzylic CH_2	"Allylic" CH_2
2	6.68 s	6.45 s	6.35 t	6.17 "t"	4.62, 4.28(AB)	4.41,4.32(AB)
3	6.68 s	6.46 s	6.42 t	6.13 t	4.49 s	4.28 d
3 + NaSCN	6.74 s	6.50 s	6.43 t	6.09 t	4.49 s	4.31 d
4	6.79 s	6.51 s	6.58 t	6.29 t	4.51 s	4.30 d
6a	6.80 s	6.45 s	6.35 t	6.18 t	4.53 s	4.34 d
6b	6.93 s	6.43 s	6.39 "t"	6.17 "t"	4.60 s	4.40 d
6c	6.79 s	6.45 s	6.37 br.	6.21 "t"	4.53 s	4.33 d
6d	6.78 s	6.48 s	6.25 t	6.06 s	4.77 s	4.50 br.
6e	6.87 s	6.49 s	6.56 t	6.23 "t"	4.51 br.	4.26 br.
5	6.87 s	6.59 s	6.74 t	6.42 t	4.52 s	4.34 d
5 + KSCN	6.69 s	6.50 s	6.43 "t"	6.29 "t"	4.50 s	4.33 "d"
7	6.75 s	6.51 s	6.29 "t"	5.99 "t"	4.67 s	4.51 d

Concerning the homologous quinhydrone **3**, which is more flexible because of its longer polyether chain, the benzylic hydrogens appear as a singlet and the allylic hydrogen atoms as a doublet as is the case with the higher homologs **4** and **5**. If a solution of the quinhydrone **3** in $CDCl_3$ is shaken with solid NaSCN the signals of the two benzoquinone, and the allylic hydrogen atoms are shifted by 0.06–0.01 pm. These minor shifts, which are reversible by using Cryptofix 221, correspond also to the minor change of the CT absorption band of **3**, which was observed in the electron spectrum after the addition of NaSCN. No shifts were detected with KSCN.

In contrast to the smaller quinhydrones **2** and **3**, the larger quinhydrones **4** and **5** exhibit the triplet of the benzoquinone hydrogen vicinal to the polyether bridge downfield-shifted in relation to the signal of the aromatic hydrogen atoms vicinal to the trimethylene bridge. This difference in the signal pattern between the pairs **4/5** and **2/3** can be explained by the fact that with the lower homologs **2** and **3** the signals of the benzoquinone hydrogens are shifted upfield by a transannular anisotropic effect of the aromatic ring due to the proximity of the donor and acceptor.

If a chloroform solution of the pentaoxa[15.3]cyclophane quinhydrone **4** is shaken with solid NaSCN the signals of the benzoquinone hydrogens are shifted considerably upfield ($\Delta\delta$ = 0.23 and 0.11, resp.). The signal of the aromatic hydrogen, being *ortho* to the trimethylene bridge, is shifted upfield only slightly ($\Delta\delta$ = 0.06), while the signal of the aromatic hydrogen, being *ortho* to the polyether bridge, and the signals of the benzylic and allylic hydrogen atoms remain almost constant. This spectrum, which is almost identical with that of the crystallized sodium complex **6a** dissolved in $CDCl_3$, reveals the same signal pattern as the tetraoxa[12.3]cyclophane quinhydrone **3**. The spectra of the sodium complexes **6a–c**, which differ only in the anion, are very similar. These upfield shifts of the benzoquinone hydrogen atoms, generated by the transannular anisotropic effect of the opposite aromatic ring, prove as well as the electron spectrum that by the conversion of the [15.3]cyclophane quinhydrone **4** into the sodium complexes **6a–c** the donor and acceptor moieties approach each other in the molecule. The complexation can be made reversible by the addition of 18-crown-16 or Cryptofix 221. Cooling a solution of the sodium complex **6a** in $CDCl_3$ or CD_2Cl_2 to 223 or 213 K, resp., causes a considerable broadening of the signals of the benzylic and allylic CH_2 groups, but not a resolution into AB systems, as is expected for a rigid structure of the quinhydrone-sodium complexes **6a**, **6b**, or **6c**. In the low-temperature spectrum at 223 K of the sodium complex **6a** there are, in addition to the slightly broadened signals of the aromatic and the benzoquinone hydrogens of **6a**, very weak signals, which may be assigned to the aromatic and the benzoquinone hydrogens of the uncomplexed quinhydrone **4**. From this it follows that in the chloroform or dichloromethane solution an equilibrium exists between the complex **6a** and a small amount of the uncomplexed quinhydrone **4** with a fast exchange process at room temperature and a slow one at 223 or 213 K. [eq. (1)]. An exchange process is also observed in an equimolar mixture of the complex **6a** and the uncomplexed quinhydrone **4**.

(quinhydrone M^+SCN^-) + quinhydrone* $\rightleftharpoons$ (quinhydrone* M^+SCN) + quinhydrone (1)

(quinhydrone M^+SCN^-) $\rightleftharpoons$ quinhydrone + M^+SCN^- (2)

The bimolecular exchange process (1) may still be superimposed by an unimolecular dissociative, solvent-dependent equilibrium [eq. (2)] lying, however, in this case on the very side of the undissociated complex **6a** because of the extremely low solubility of NaSCN in chloroform or dichloromethane. Since the $CDCl_3$ employed for the NMR spectroscopy always contains traces of water the small amount

of **4** observed during the dissolution of the sodium complex **6a** may originate from decomplexation according to eq. (2). The existence of a very small amount of the quinhydrone **4** as impurity in the sodium complex **6a**, however, cannot be completely excluded.

With the quinhydrone-calcium complex **6d** dissolved in $CDCl_3$ the benzoquinone hydrogen signals are shifted by 0.33 and 0.23 ppm, resp., and are thus shifted further upfield than in the sodium complexes **6a–c**. This stronger transannular anisotropic effect of the opposite aromatic ring indicates an even closer approach of the donor and acceptor moieties. This is proven by NOE difference spectra. Irradiations of the aromatic and the benzoquinone hydrogens of the complex **6d** produced signal enhancements of the transannularly opposite benzoquinone and aromatic hydrogens and consequently postulate a pseudogeminal arrangement of the donor and acceptor components in analogy to the [3.3]paracyclophane quinhydrone **1a**. At room temperature the signal of benzylic CH_2 group is a sharp singlet, that of the allylic hydrogen is broadened and the 6 hydrogen atoms of the trimethylene bridge show a single, very broad signal. At 328 K this very broad signal splits into 3 broad signals, and the signal of the allylic CH_2 hydrogens becomes sharper. On cooling to 243 K the situation parallels that of the sodium complex **6a**. In addition to the 4 signals of the aromatic and the benzoquinone hydrogens of the complex **6d** very weak signals of the uncomplexed quinhydrone **4** (ratio 1:9) arise. The benzylic and the allylic CH_2 hydrogens are now exhibited as clearly discernible AB systems at δ = 4.69, 4.83 and 4.34, 4.63, resp., as is expected for a rigid structure. The singlet observed at δ = 4.96 is presumably generated by coordinated water. The 6 hydrogen atoms of the trimethylene bridge are displayed as 6 separate multiplets. Also in CD_2Cl_2 at 243 K the benzylic as well as the allylic CH_2 group appear as AB systems. By a ROESY[*] spectrum in $CDCl_3$ at 243 K of a mixture of the calcium complex **6d** and the quinhydrone **4** in a ratio of 2:1 it was proven that in the solution of **6d** in $CDCl_3$ – in analogy to the sodium complex **6a** – a rapid exchange at room temperature, but a slow one at low temperature [eq. (1)] takes place between the complex and a small amount of the uncomplexed compound **4**. The fact that in the case of the calcium complex at 243 K the signals of both the complexed and the uncomplexed species are substantially more distinct than those with the sodium complex, is explained by different rates of the exchange processes.

The mercury complex **6e** reveals in $CDCl_3$ at room temperature broadened signals for the benzylic and the allylic CH_2 groups as well as the for the 3 CH_2 groups of the trimethylene bridge. At 328 K, however, these signals become sharper, and some of them are split. The signal patterns of the aromatic and the benzoquinone hydrogens in **6e** differ remarkably from those of the sodium and the calcium complex, but resemble more that of the uncomplexed quinhydrone **4**. Also the upfield shifts of the benzoquinone hydrogens ($\Delta\delta$ = 0.02 and 0.06, resp.) are small compared to those of **6a–c**. Consequently, the donor and the acceptor components in the mercury complex **6e** do not approach each other as closely as in the sodium and calcium complexes **6a–d**. Analogously to **6a** and **6d** at 243 and 223 K in addition to the signals of the aromatic and the benzoquinone hydrogens of the complex **6e** very weak signals of the uncomplexed compound **4** are observed. Furthermore, the hydrogens of the benzylic and the allylic CH_2 group are now detected as AB systems and the hydrogens of the trimethylene bridge as 6 separate signals.

If a chloroform solution of the [15.3]paracyclophane quinhydrone **4** is shaken with KSCN or $Ba(SCN)_2$ hardly any change in the NMR spectrum is observed. However, the larger [18.3]paracyclophane quinhydrone **5** shows a considerable effect with KSCN. Among the signals of the aromatic and the benzoquinone hydrogens the benzoquinone hydrogen vicinal to the polyether bridge reveals the strongest upfield shift ($\Delta\delta$ = 0.31). Even larger are the signal shifts of the barium complex **7**. The upfield shifts of the benzoquinone hydrogens ($\Delta\delta$ = 0.45 and 0.43, resp.) and the downfield shifts of the benzylic and the allylic hydrogens ($\Delta\delta$ = 0.15 and 0.17) are especially striking. Cooling to 213 K produces a signal broadening of the benzylic and the allylic CH_2 hydrogens, but no splitting into AB systems.

Amongst the spectra of the tetramethoxyoligooxa-[3*n*.3]paracyclophanes **8–11** (Table 3) that of the lowest homolog, the [9.3]paracyclophane **8**, is the most complex one.

Table 3. ^{1}H-NMR signals of the tetramethoxyoligooxa[3*n*.3]paracyclophanes **8–11** in $CDCl_3$ and their shifts caused by alkali thiocyanates

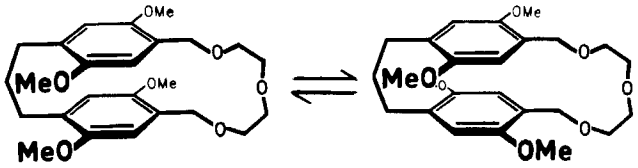
Comp.	Aromat. H ortho to $(CH_2OCH_2)_n$	Aromat. H ortho to $(CH_2)_3$	Benzylic CH_2
8a + **8b**	6.57 (**8a**)	6.27 (**8a**)	4.64, 4.31 AB (**8a**)
	6.41 (**8b**)	6.53 (**8b**)	4.63, 4.27 AB (**8b**)
9	6.69	6.44	4.50
9 + NaSCN	6.74	5.98	4.41
9 + KSCN	6.72	6.38	4.44
10	6.87	6.61	4.56
10 + NaSCN	6.68	6.41	4.52
10 + KSCN	6.83	6.47	4.53
11	6.91	6.67	4.57
11 + NaSCN	6.75	6.55	4.52
11 + KSCN	6.79	6.57	4.55

If a crystal, which has been unambiguously identified by X-ray analysis as pseudogeminal tetramethoxy-2,5,8-trioxa-[9.3]paracyclophane **8a**, is dissolved in $CDCl_3$, two signal pairs of aromatic hydrogens (ratio 4:3) instead of one appear. The two weaker signals are located between the two stronger ones.

Comparing the signals of the aromatic hydrogens *ortho* to the trimethylene bridge with those of the aromatic hydrogens of the pseudogeminal and pseudoortho tetramethoxy-[3.3]paracyclophane (δ = 6.21 and 6.40, resp.)[2b], we can tentatively assign the stronger signal at δ = 6.27 to the pseudogeminal **8a**, while we assign the weaker one at δ = 6.53 to a pseudoortho **8b**. The existence of bridge conformers, however, cannot be excluded. In [D_6]DMSO also two signal pairs of aromatic hydrogens, however at a ratio of

[*] *R*otating Frame *O*verhauser *E*nhancement *S*pectroscopy.

2:1, are detected. On raising the temperature from 304 to 373 K the inner signals become a little stronger at the expense of the outer signals and move closer together. This change is reversible by cooling to room temperature. Presumably, there exists a slowly adjusting temperature-dependent equilibrium between the forms **8a** and **8b**.



8a **8b**

The signals of benzylic hydrogens of **8a** and **8b** are of the AB type. Position and number of the signals of the trimethylene hydrogens of **8a** and **8b** are very similar to the corresponding ones of the pseudogeminal and the pseudoortho tetramethoxy[3.3]paracyclophanes[2b].

In the spectra of the larger tetramethoxyparacyclophanes **9**–**11** the signals of the two aromatic hydrogens and to a smaller extent those of the benzylic hydrogens are shifted downfield with increasing size of the macrocycle. Upon shaking of the chloroform solution of the [12.3]paracyclophane **9** with NaSCN the signal of the aromatic hydrogen *ortho* to the trimethylene group is shifted considerably upfield ($\Delta\delta$ = 0.46). No characteristic changes were detected by treatment of **9** with KSCN.

Also upfield shifts ($\Delta\delta$ = 0.19 and 0.20, resp.) of the aromatic hydrogens were observed by treatment of tetramethoxypentaoxa[15.3]paracyclophane **10** with NaSCN, suggesting a stacking of the two aromatic rings. The effect of the potassium is weaker ($\Delta\delta$ = 0.04 and 0.14, resp.). In the higher homolog **11** potassium ions ($\Delta\delta$ = 0.12 and 0.10, resp.) and sodium ions ($\Delta\delta$ = 0.16 and 0.12, resp.) display an approximately equally strong upfield shift of the signals of the aromatic hydrogens.

Molecular Structures

Molecular Structure of the Calcium Complex 6d

The side view of the molecular structure (Figure 3 above) reveals that the 15-membered polyether bridge wraps itself – similar to a puckered crown ether ring – around the calcium ion which is coordinated sevenfold by the 5 ether oxygens of the bridge and the nitrogen atoms of the two thiocyanato groups. The calcium ion derivates only by 3.7(1) pm from the mean O_5 plane. Both thiocyanate ions are positioned above and below the O_5 plane, their bond distances via the nitrogen atoms to the calcium ion are almost of the same length and, due to the ionic character of the bond, slightly shorter than the coordinative bonds between calcium and the ether oxygens of the bridge. The mean Ca···O and Ca···N bond distance is 245(4) and 235(1) pm, resp. Compared to those of the 15-membered crown-5-$Ca(SCN)_2$ complex[10a] [254(3) and 247(4) pm, resp.] they are even shorter. (In the 15-crown-5 complex the calcium ion is situated above the O_5 plane and is coordinated on the same side by a molecule of water as well as by the two thiocyanate ions.) The polyether bridge from C(1) to C(15) has almost C_s symmetry (Figure 3 below). The O_5 plane is nearly perpendicular to the benzene and the benzoquinone plane (85 and 83°, resp.) and is, presumably for steric reasons, turned away from the vicinal methoxy and carbonyl group (Figure 3 below).

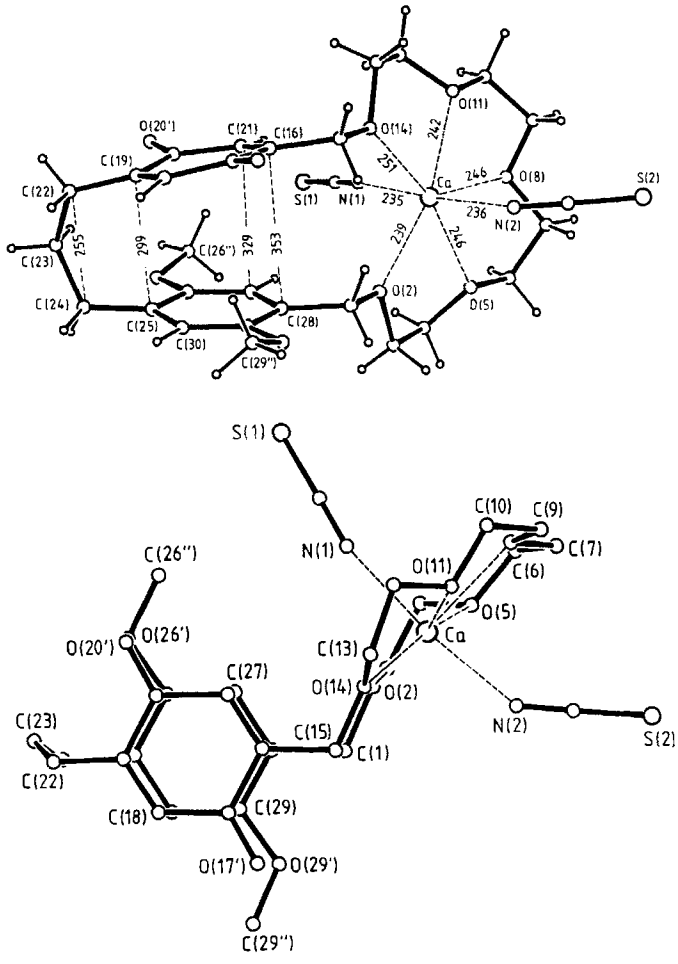


Figure 3. Molecular structure of the calcium complex **6d**: above side view, below top view

The top view of the molecular structure shows the orientation of the donor and acceptor components being very similar to that in the pseudogeminal structure **1a**, namely the almost ecliptic positions of the carbon atoms and the oxygen functions of the two six-memberd rings. The distance between the bridgehead atoms C(19) to C(25) at the trimethylene bridge is as short as in **1a** (302 pm). Also, the distance between the two ring centers (328 pm) is very similar to that in **1a** (319 pm). The distances between the ring carbon atoms C(20) and C(26) with 312 pm and between the carbonyl oxygen O(20') and the methoxy oxygen O(26') with 313 pm are also optimal for a CT complex. As the macrocycle expands towards the complexed polyether bridge the distances between the polyether bridgehead atoms C(16) and C(28) as well as that between the neighboring atoms C(15) and C(1) (353 and 369 pm, resp.) and

that of the carbonyl and the methoxy group near the polyether bridge [O(17′)···O(29′] = 390 pm) are larger. The *para* axis of the benzoquinone and the aromatic ring form an angle of 11°. The planes of the aromatic ring and the benzoquinone [C(18)−C(19)−C(21)−C(16)] form an angle of 12.6°. The two methoxy groups are turned out from the plane of the aromatic ring by 11° [C(27)−C(26)−O(26′)−C(26″)] and 18° [C(30)−C(29)−O(29′)−C(29″)], resp., towards the benzoquinone ring. Whereas the aromatic ring is completely planar the benzoquinone ring is slightly deformed to give a boat-like structure as was also found in **1a**. Due to a stronger transannular interaction [shorter transannular distance of C(20)···C(26) in comparison with C(17)···C(29)] the plane C(19)−C(20)−C(21) is with 8.9° more bent out of the benzoquinone plane than the plane C(16)−C(17)−C(18) with 5.4°. Furthermore, the benzoquinone ring is tilted along the *para* axis by approximately 4° in such a way that the benzoquinone atoms C(20), O(20′), and C(21) are closer to the aromatic ring than the atoms C(17), O(17′), and C(18).

Molecular Structure of the Mercury Complex 6e

The side view of the molecular structure (Figure 4 above) reveals a macrocycle, which, despite complexation with the mercury ion, is relatively strongly expanded towards the polyether bridge. The mercury ion is coordinated by the 5 oxygens of the polyether bridge and because of its "soft character" by the sulfur atoms of the two thiocyanate ions, which lie above and below the O_5 plane. It deviates by only 1.6 (1) pm from the least-squares plane through the 5 oxygens of the bridge. The bond distances between the mercury ion and the polyether oxygens correspond to those in the mercury complex of a diphenyl polyether system with two $(CH_2OCH_2)_5$ bridges[5b]. The particularly long Hg···O(14) bond (305 pm) favors a strong libration (tumbling motion) of the benzoquinone ring. An exact determination of the bond lengths and bond angles in the benzoquinone from O(14) to C(23) is therefore not possible (disorder). The polyether bridge from O(2) to O(14) has approximately C_s symmetry. The bonds between the mercury ion and the sulfur atoms of the two thiocyanate ions are almost of the same length, however considerably shorter than the Hg···O bond distances. The O_5 plane is almost perpendicular (87°) to the aromatic ring, which including the methoxy group is completely planar. The aromatic and the benzoquinone plane enclose an angle of 25.6°. The distance between the two six-membered rings is over 400 pm. From the top view (Figure 4 below) it becomes obvious that the donor-acceptor arrangement corresponds to a pseudoortho structure with the six-memberd rings moved sideways. The *para* axis of the benzoquinone ring projected to the plane of the aromatic ring forms an angle of 27° with the *para* axis of that plane.

Molecular Structure of the Barium Complex 7

The 6 oxygen atoms of the 18-membered polyether bridge form a ring around the barium ion (Figure 5 above), which

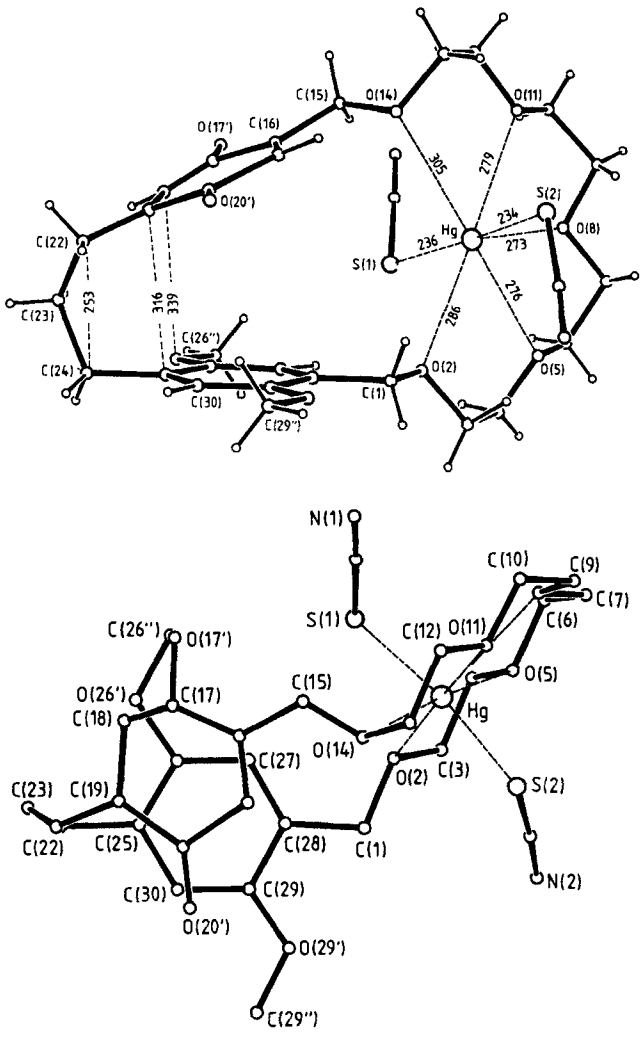


Figure 4. Molecular structure of the mercury complex **6e**: above side view, below top view

is coordinated eightfold and positioned within the O_6 plane with only slightly differing Ba···O bond lengths. The polyether loop forms a puckered, crown ether-like ring by crossing the bonds O(2)−C(3) and C(16)−O(17) (Figure 5 below). The mean Ba···O bond length of 286(4) pm is almost identical with the mean bond length of 284(2) pm found in the 18-crown-6-barium thiocyanate complex $C_{12}H_{24}O_6 \cdot Ba(SCN)_2 \cdot H_2O$[10b]. The barium ion in this complex, however, on one side is coordinated by the two thiocyanate ions and on the opposite side by a water molecule, whereas in **7** one thiocyanate ion lies above and the other one below the O_6 plane. The torsion angles C−C−O−C and O−C−C−O of the coordinated polyether loop with alternating *aga* units (*a* = *anti*, *g* = *gauche*) correspond to those of the 18-crown-6 barium complex. The polyether bridge from C(1) to C(18) has almost C_2 symmetry. The donor and acceptor components are fixed in an orientation which corresponds to a pseudoortho structure with divering *para* axes of the two six-membered rings. The projection of the *para* axis of the benzoquinone ring C(19)···C(22) onto the aromatic plane (Figure 5 below) forms with the *para* axis of the latter an

angle of 25°. In this projection the distance between the centers of the two six-membered rings is 110 pm. The macrocycle is expanded towards the polyether loop. Therefore, the bridgehead atoms C(19) and C(31) are further away from each other than C(22) and C(28), which are linked with the trimethylene bridge. The distance of the latter (309 pm) is very similar to the corresponding distance (302 pm) found in the pseudogeminal **1a**. The center of the benzoquinone ring is 336 pm above the aromatic plane. The *para* axis of the benzoquinone ring C(19)···C(22) is inclined to the aromatic plane by 10° whereas the benzoquinone ring is tilted around this axis towards the aromatic ring by 4°.

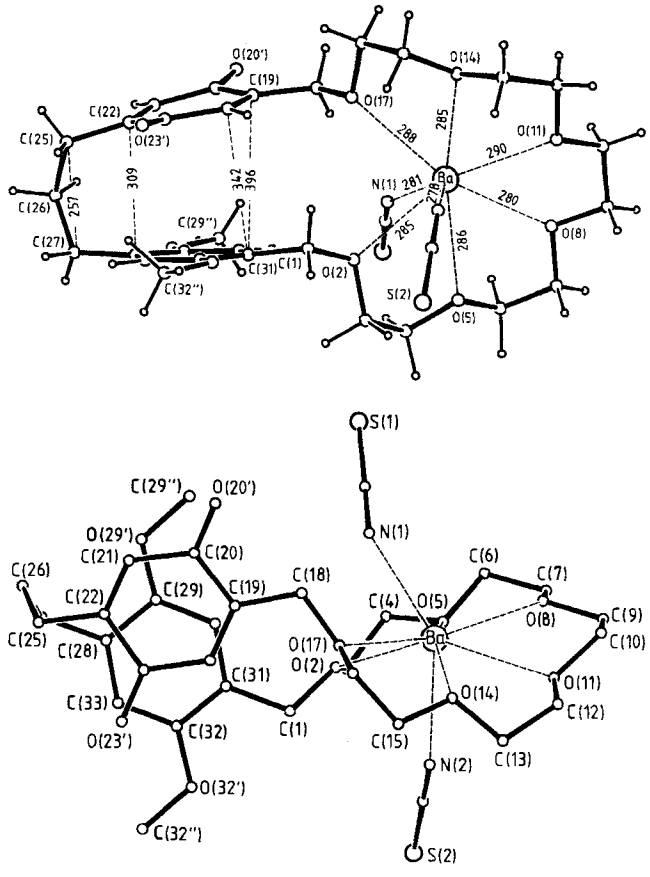


Figure 5. Molecular structure of the barium complex **7**: above side view, below top view

The methoxy groups are only slightly turned outward of the aromatic plane namely C(30)–C(29)–O(29')–C(29'') by 6° towards the benzoquinone ring and C(33)–C(32)–O(32')–C(32'') by 8° away from the benzoquinone ring. While the aromatic ring is planar, the benzoquinone ring is slightly deformed to a boat-like structure. Relative to the plane of the four middle C atoms C(19), C(24), C(22), C(21) both the triangular planes C(19)–C(20)–C(21) and C(22)–C(23)–C(24) are turned outward by 6.9 and 8.1°, resp. With the O_6 plane of the polyether loop the aromatic and the benzoquinone ring form a dihedral angle of 76.2 and 82.4°, resp. There are still some interesting angle deformations in the benzoquinone ring. The angle C(1)–C(31)–C(30) centered at the bridgehead atom C(31) of the aromatic ring is with 121.5° only slightly expanded compared to the angle C(1)–C(31)–C(32) with 120.1°, while the expansion of the angle C(18)–C(19)–C(24) with 125.2° is remarkable compared to the angle C(18)–C(19)–C(20) with 116.4°. Similar strong angle deformations were encountered on the bridgehead atom C(22) with an expansion of the angle C(21)–C(22)–C(25) by 124.0° compared to 118.3° of the angle C(23)–C(22)–C(25).

Molecular Structure of the Tetramethoxytrioxa[9.3]paracyclophane 8a

The macrocycle of **8a** is expanded towards the polyether chain (Figure 6 above). The two planes C(11)–C(12)/C(14)–C(15) and C(20)–C(21)/C(23)–C(24) of the aromatic rings enclose an angle of 15°. Both aromatic rings, whose arrangement corresponds to the pseudogeminal type, are displaced horizontally around the trimethylene bridge as axis (Figure 6 below). The *para* axes form an angle of 25°. Relatively short transannular distances are found only in the region of the bridgehead atoms of the trimethylene bridge (Figure 6 above). The distances between the rings near the polyether chain amount to 364 pm for C(11)···C(21), 367 pm for C(11)···C(22) and 386 pm for C(10)···C(21). Both aromatic rings are slightly bent away from each other. The triangular planes C(12)–C(13)–C(14) and C(11)–C(10)–C(15) of ring B are turned inwards by 3.3 and 1.6°, resp., the triangular planes C(20)–C(19)–C(24) and C(21)–C(22)–C(23) of ring A by 2.8 and 0.6°, resp., and the bonds C(10)–C(9) and C(22)–C(1) by 1 and 3.5°, resp. Ring B is tilted by 5° around the *para* axis towards ring A. The vibration parameters indicate that the trimethylene bridge is relatively fixed, while the polyether bridge is flexible.

Molecular Structure of the Benzoquinonophane 20

The molecular structure shows a dent from O(8) to O(11), indicating the tendency of the polyether bridge to fill the lumen of the macrocycle. Therefore, the arrangement of the 15-membered polyether bridge is entirely different from that in the quinhydrone calcium complex **6d** or the quinhydrone mercury complex **6e**. Figure 7 shows the interesting feature of the two benzoquinone rings being almost vertical to each other. The distance of the centers of the two benzoquinone rings is more than 600 pm.

Acyclic Quinhydrones

The quinhydrones **21**–**24** containing only one trimethylene bridge and the quinhydrones **25**–**27** containing a polyether bridge were synthesized in order to determine whether the intramolecular interaction between the benzoquinone and the dimethoxyphenyl components also takes place in acyclic systems. Furthermore, it was tested whether the compounds with relatively long polyether bridges would indicate an approach of the donor and acceptor moieties by coordination of the ether oxygens of the bridge with metal ions inducing a CT interaction as in the oligooxaparacyclophane quinhydrone-metal complexes **6a**–**e** and **7**.

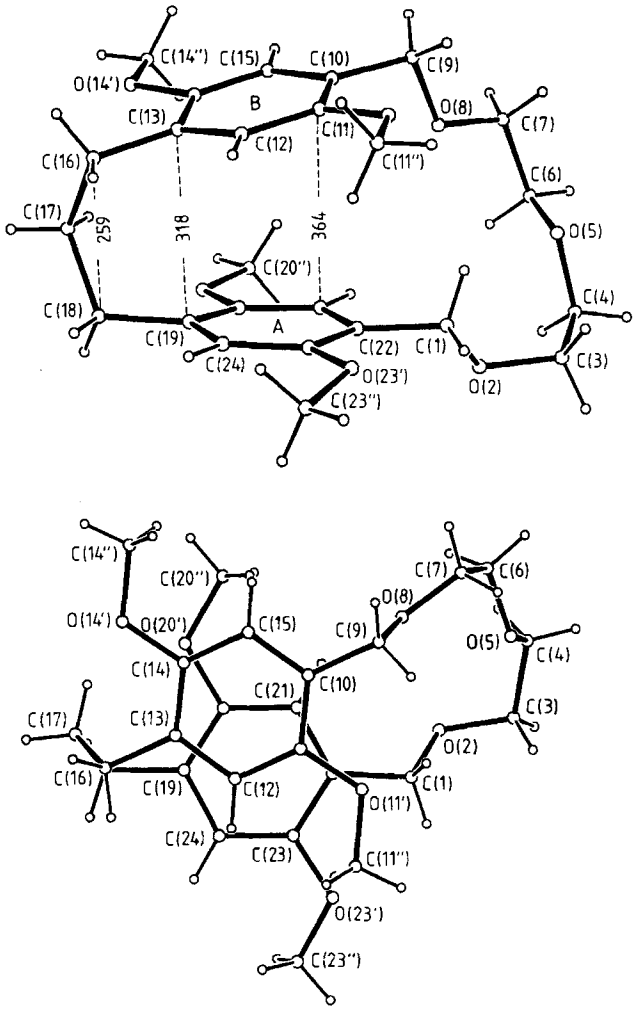


Figure 6. Molecular structure of the tetramethoxytrioxa[9.3]paracyclophane **8a**: above side view, below top view

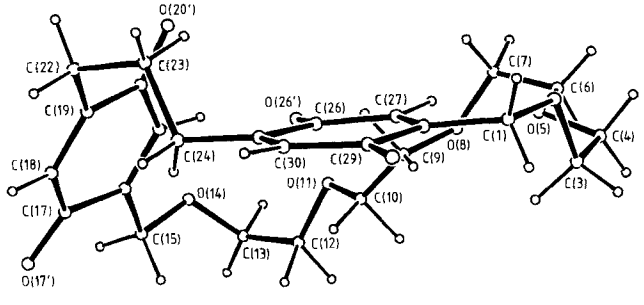
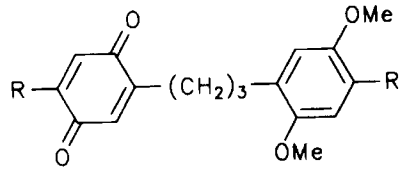
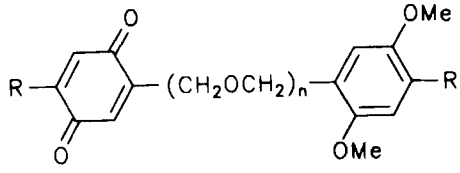


Figure 7. Molecular structure of the pentaoxa[15.3]benzoquinonophane **20**

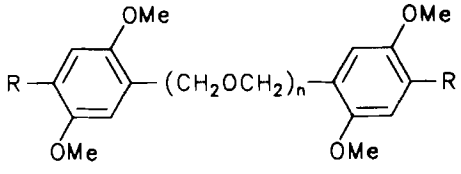
The partial oxidative demethylation of 1,3-bis(2,5-dimethoxyphenyl)propane (**12**) and of the dimethyl, bis(methoxymethyl) and bis(ethoxyethyl) derivatives **17**–**19** leading to the acyclic 2-[(2,5-dimethoxyphenyl)propyl]benzoquinones **21**–**24** was carried out analogously to the conversion of the cyclic tetramethoxyoligooxa[3*n*.3]paracyclophanes. The same method was also used for the oxidative demethylation of the bis(2,5-dimethoxyphenyl)oligooxaalkanes **28**–**32**. While 2-[9-(2,5-dimethoxyphenyl)-2,5,8-trioxanonyl]benzoquinone (**25**) and 2-[12-(2,5-dimethoxyphenyl)-2,5,8,11-tetraoxadodecyl]benzoquinone (**26**) were obtained from the tetramethoxy compounds **28** and **29**, resp., the deeply red [15]- and [18]diphenoquinonophanes **33**[11] and **34**[11] were formed from the larger tetramethoxy compounds **30**[12] and **32**, resp.



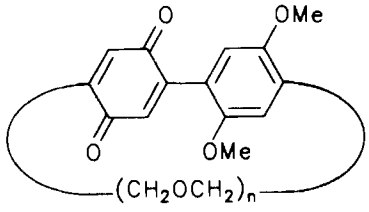
21: R = H
22: R = CH_3
23: R = CH_2OMe
24: R = CH_2OEt



25: n = 3, R = H
26: n = 4, R = H
27: n = 5, R = CH_3



28: n = 3, R = H
29: n = 4, R = H
30: n = 5, R = H
31: n = 5, R = CH_3
32: n = 6, R = H



33: n = 5
34: n = 6

If, however, the aromatic hydrogen atoms *para* to the polyether bridge of **30** are replaced by methyl groups, only the benzoquinone derivatives can be obtained. Thus, the acyclic quinhydrone **27** was synthesized from the corresponding tetramethoxy compound **31**. This indicates the position of the connection of the two six-membered rings in the macrocyclic diphenoquinone derivatives, whose structures were also verified by the ^{1}H-NMR data and a comparison of the UV/Vis spectra with the spectrum of the known 2,5-

dimethoxy-4,4'-dimethyl-1,1'-di-2',5'-phenoquinone (λ_{max} in EtOH: 460, 290 and 240 nm)[13].

The electron spectra of the quinhydrones **21**–**24** show in the visible region only shoulders at 445 nm with ε values <100, which are not changed by addition of NaSCN or KSCN. Under these weak absorptions the portion of the n-π* transition of the benzoquinone chromophore compared to the CT effect is relatively high.

Also the acyclic polyether-bridged donor-acceptor systems **25**–**27** show only absorptions in the visible spectrum, not indicating any clearly established intramolecular CT interactions. The intensity of the absorption rises, however, at 440 nm upon the addition of NaSCN or KSCN to solutions in chloroform of **26** (with NaSCN from ε = 60 to 94, with KSCN to ε = 68) and of **27** (with NaSCN from ε = 42 to 103, with KSCN to ε = 70). But these effects are, in comparison with those of the cyclic quinhydrones **4** and **5**, very weak[14].

Experimental

UV/Vis: Cary 17 and 2300, resp. – ^{1}H NMR: Bruker WP 80, HX 360, and AM 500. – MS: Dupont 21–492, Finnigan MAT 212, and VG ZAB2E. – IR: Beckman spectrophometer 4240. – Chromatography: Column of silica gel Silitech 60–200 mesh, 60 Å, ICN Biochemicals, DC with microcards Si F, Riedel-de Haën. – Melting points: Bock Monoscope (uncorrected). – Cyclizations: Two-Components Dilution Method Equipment according to Vögtle. – Purification of the commercial sodium hydride oil dispersion by slurrying three times with anhydrous THF and decanting.

20,23-Dimethoxy-2,5,8-trioxa[9](2,5)-p-benzoquinono[3]paracyclophane (**2**): A solution of 490 mg (0.89 mmol) of diammonium hexanitratocerate in 10 ml of water was added dropwise to a stirred solution of 200 mg (0.45 mmol) of tetramethoxytrioxa[9.3]paracyclophane **8** in 40 ml of acetonitrile. After 30 min the solution was shaken three times with dichloromethane/water (1:1). The combined organic phases were dried with $MgSO_4$ and concentrated in vacuo. Chromatography of the orange-red, oily residue over silica gel with ethyl acetate/cyclohexane (1:2) yielded 87 mg (48%) of orange-red crystals with mp 120–122°C. – UV/Vis ($CHCl_3$): λ_{max} (ε) = 467 nm (540), 290 sh (5123), 258 (15243). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.00–2.09 [m, 1H, $(CH_2)_3$], 2.29–2.38 [m, 2H, $(CH_2)_3$], 2.39–2.46 [m, 1H, $(CH_2)_3$], 2.47–2.54 [m, 1H, $(CH_2)_3$], 3.01–3.09 [m, 1H, $(CH_2)_3$], 3.64–3.85 [m, 14H, $O(CH_2CH_2O)_2$ + 2 OCH_3], 4.32, 4.41 (ABX, J_{AB} = 17, J_{AX} = 2.2 Hz, 2H, allylic CH_2), 4.28, 4.62 (AB, J = 13 Hz, 2H, benzylic CH_2), 6.17 ("t", 1H, benzoquinone H), 6.35 (X part of ABX, J_{BX} = 2.2 Hz, 1H, benzoquinone H), 6.45 (s, 1H, aromatic H), 6.68 (s, 1H, aromatic H). – IR (film): $\tilde{\nu}$ = 1640 cm^{-1} br., 1650 sh (νC=O). – MS (170–180°C), *m/z*: 416 [M^+] (100%). – $C_{23}H_{28}O_7$ (416.5): calcd. C 66.33, H 6.78; found C 66.27, H 6.82.

23,26-Dimethoxy-2,5,8,11-tetraoxa[12](2,5)-p-benzoquinono[3]paracyclophane (**3**): Preparation by analogy with **2** from 200 mg (0.41 mmol) of tetramethoxytetraoxa[12.3]paracyclophane **9** in 40 ml of acetonitrile and 490 mg (0.89 mmol) of diammonium hexanitratocerate in 10 ml of water. After chromatography of the orange, oily crude material over silica gel with ethyl acetate/cyclohexane (3:1) 120 mg (65%) of orange crystals with mp 68–70°C (*n*-heptane) was obtained. – UV/Vis ($CHCl_3$): λ_{max} (ε) = 467 nm (495), 293 (4610), 257 (14100). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.16 (m, 2H, $CH_2CH_2CH_2$), 2.47 (m, 2H, $CH_2CH_2CH_2$ at the benzoquinone), 2.69 (m, 2H, $CH_2CH_2CH_2$ at the aromat), 3.67–3.76 [m, 18H, 2 OCH_3 + $O(CH_2CH_2O)_3$, 3.68, OCH_3 vicinal to $(CH_2)_3$, 3.70, OCH_3 *ortho* to $(CH_2OCH_2)_4$], 4.28 (d, J = 2.1 Hz, 2H, allylic CH_2), 4.49 (s, 2H, benzylic CH_2), 6.13 [t, J = 1.3 Hz, 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.42 [t, J = 2.1 Hz, 1H, benzoquinone H vicinal to $(CH_2OCH_2)_4$], 6.46 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.68 [s, 1H, aromatic H *ortho* to $(CH_2OCH_2)_4$]; assignment by H/H-COSY. – IR (film): $\tilde{\nu}$ = 1645 cm^{-1}, 1650 sh (νC=O). – MS (220–230°C), *m/z*: 460 [M^+] (100%). – $C_{25}H_{32}O_8$ (460.5): calcd. C 65.20, H 7.00; found C 65.08, H 6.86.

26,29-Dimethoxy-2,5,8,11,14-pentoxa[15](2,5)-p-benzoquinono[3]paracyclophane (**4**): Preparation by analogy with **3** from 120 mg (0.22 mmol) of tetramethoxypentaoxa[15.3]paracyclophane **10** in 20 ml of acetonitrile and 310 mg (0.57 mmol) of diammonium hexanitratocerate in 5 ml of water. Yield after chromatography 110 mg (97%) of an orange-red oil, which after treatment with diethyl ether crystallized as orange-red prisms with mp 71–72°C, after recrystallization from *n*-heptane mp 72–73°C. – UV/Vis ($CHCl_3$): λ_{max} (ε) = 462 nm (324), 293 (5465), 254 (14970). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 2.03 (quint, J = 7 Hz, 2H, $CH_2CH_2CH_2$), 2.43 (t, J = 7 Hz, 2H, $CH_2CH_2CH_2$ at the benzoquinone), 2.66 (t, J = 7 Hz, 2H, $CH_2CH_2CH_2$ at the aromat), 3.60–3.72 [m, 22H, 2 OCH_3 + $O(CH_2CH_2O)_4$, 3.69, OCH_3 vicinal to $(CH_2)_3$, 3.72, OCH_3 *ortho* to $(CH_2OCH_2)_5$], 4.30 (d, J = 2 Hz, 2H, allylic CH_2), 4.51 (s, 2H, benzylic CH_2), 6.29 [t, J = 1.2 Hz, 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.51 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.58 [t, J = 2 Hz, 1H, benzoquinone H vicinal to $(CH_2OCH_2)_5$], 6.79 [s, 1H, aromatic H *ortho* to $(CH_2OCH_2)_5$]; assignment by H/H-COSY. – IR (film): $\tilde{\nu}$ = 1645 cm^{-1} br. (νC=O). – MS (270–280°C), *m/z*: 504 [M^+] (100%). – $C_{27}H_{36}O_9$ (504.9): calcd. C 64.27, H 7.19; found C 64.27, H 7.24.

29,32-Dimethoxy-2,5,8,11,14,17-hexaoxa[18](2,5)-p-benzoquinono[3]paracyclophane (**5**): Preparation by analogy with **3** from 1.955 g (3.38 mmol) of tetramethoxyhexaoxa[18.3]paracyclophane **11** in 60 ml of acetonitrile and 3.78 g (6.90 mmol) of diammonium hexanitratocerate in 10 ml of water. Chromatography of the orange, oily crude material yielded 1.47 g (75%) of yellow crystals with mp. 88–90°C. – UV/Vis ($CHCl_3$): λ_{max} (ε) = 442 nm (213), 293 (5340), 254 (18030). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.92 ("quint", J = 7 Hz, 2H, $CH_2CH_2CH_2$), 2.42 (dt, J_d = 1.2, J_t = 7 Hz, $CH_2CH_2CH_2$ at the benzoquinone), 2.66 (t, J = 7 Hz, 2H, $CH_2CH_2CH_2$ at the aromat), 3.60–3.69 [m, 20H, $O(CH_2CH_2O)_5$], 3.72 [s, 3H, OCH_3 *ortho* to $(CH_2)_3$], 3.75 [s, 3H, OCH_3 *ortho* to $(CH_2OCH_2)_6$], 4.34 (d, J = 2 Hz, 2H, allylic CH_2), 4.52 (s, 2H, benzylic CH_2), 6.42 [t, J = 1.3 Hz, 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.59 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.74 [t, J = 2 Hz, 1H, benzoquinone H vicinal to $(CH_2OCH_2)_6$], 6.87 [s, 1H, aromatic H *ortho* zu $(CH_2OCH_2)_6$]; assignment by H/H-COSY. – IR (KBr): $\tilde{\nu}$ = 1640 cm^{-1} (νC=O). – MS (370–380°C), *m/z* (%): 548 [M^+] (10), 177 (100). – $C_{29}H_{40}O_{10}$ (548.6): calcd. C 63.49, H 7.35; found C 63.78, H 7.60.

[26,29-Dimethoxy-2,5,8,11,14-pentaoxa[15](2,5)-p-benzoquinono[3]paracyclophane]sodium Thiocyanate (**6a**): A solution of 100 mg (0.20 mmol) of pentaoxa[15.3]paracyclophane quinhydrone **4**, 15.0 mg (0.19 mmol) of NaSCN, and 0.5 ml of triethyl orthoformate in 20 ml of anhydrous acetone was refluxed for 5 min. After cooling of the solution to room temp. 20 ml of diethyl ether was added to give 61.5 mg (57%) of the sodium complex as red crystals, which were dried in vacuo at 70°C, mp 152–153°C (dec.). The sodium complex could also be reprecipitated from ethyl acetate with diethyl ether. – UV/Vis ($CHCl_3$): λ_{max} (ε) = 480 nm (996), 296 (4460), 258 sh (12430). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.19 (mc, 2H, $CH_2CH_2CH_2$), 2.48 (t, J = 6 Hz, 2H, $CH_2CH_2CH_2$ at the benzoquinone), 2.68 (t, J = 6 Hz, 2H, $CH_2CH_2CH_2$ at the aromat), 3.60–3.80 [m, 22H, 2 OCH_3 + $O(CH_2CH_2O)_4$, 3.70, s, OCH_3 *ortho* to $(CH_2OCH_2)_5$, 3.79, s, OCH_3 vicinal to $(CH_2)_3$], 4.34 (d, J = 2 Hz, 2H, allylic CH_2), 4.53 (s, 2H, benzylic CH_2), 6.18 ["t", 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.35 [t, J = 2 Hz, 1H, benzoquinone H vicinal to $(CH_2OCH_2)_5$], 6.45 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.80 [s, 1H, aromatic H *ortho* to $(CH_2OCH_2)_5$]; assignment by H/H-COSY and NOE difference spectrum (NOED). – IR (KBr): $\tilde{\nu}$ = 2070, 2060 cm^{-1} (νNCS), 1650 (νC=O). – MS (FAB, *m*-nitrobenzyl alcohol + 1% CF_3CO_2H), *m/z*: 527 [M^+ – NCS] (100%). – $C_{28}H_{36}NNaO_9S$ (585.7): calcd. C 57.42, H 6.20, N 2.39; found C 57.47, H 5.99, N 2.19.

[26,29-Dimethoxy-2,5,8,11,14-pentaoxa[15](2,5)-p-benzoquinono[3]paracyclophane]sodium Iodide (**6b**): Preparation by analogy with **6a** from 100 mg (0.20 mmol) of **4** and 27.0 mg (0.18 mmol) of sodium iodide (dried in vacuo). Layering of the acetone solution with diethyl ether yielded 41 mg (35%) of red needles, which were dried at 50°C in vacuo, mp 188°C. – UV/Vis ($CHCl_3$): λ_{max} (ε) = 479 nm (959), 296 (4585). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.19 [mc, 2H, $(CH_2)_3$], 2.47 [t, J = 6 Hz, 2H, $(CH_2)_3$], 2.68 [t, J = 6 Hz, 2H, $(CH_2)_3$], 3.60–3.90 [m, 22H, 2 OCH_3 + $O(CH_2CH_2O)_4$], 4.40 (d, J = 2 Hz, 2H, allylic CH_2), 4.60 (s, 2H, benzylic CH_2), 6.17 ("t", 1H, benzoquinone H), 6.39 ("t", 1H, benzoquinone H), 6.43 (s, 1H, aromatic H), 6.93 (s, 1H, aromatic H). – IR (KBr): 1650 cm^{-1} (νC=O). – $C_{27}H_{36}INaO_9$ (654.5): calcd. C 49.55, H 5.54, I 19.39; found C 49.29, H 5.56, I 19.48.

[26,29-Dimethoxy-2,5,8,11,14-pentaoxa[15](2,5)-p-benzoquinono[3]paracyclophane]sodium Perchlorate (**6c**): Preparation by analogy with **6a** from 102 mg (0.20 mmol) of **4** and 27.0 mg (0.19 mmol) of sodium perchlorate monohydrate. Yield: 32 mg (27%) of red crystals, mp 200–203°C. – UV/Vis ($CHCl_3$: λ_{max} (ε) = 478 nm (918), 295 (4490), 258 (12700). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.15 [mc, 2H, $(CH_2)_3$], 2.47 [t, J = 6.1 Hz, 2H, $(CH_2)_3$], 2.68 [t, J = 6.1 Hz, 2H, $(CH_2)_3$], 3.66–3.80 [m, 22H, 2 OCH_3 + $O(CH_2CH_2O)_4$, 3.69, s, OCH_3 *ortho* to $(CH_2OCH_2)_5$, 3.72, s, OCH_3 vicinal to $(CH_2)_3$], 4.33 (d, J = 1.8 Hz, 2H, allylic CH_2), 4.53 (s, 2H, benzylic CH_2), 6.21 ["t", 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.37 [br, 1H, benzoquinone H vicinal to $(CH_2OCH_2)_5$], 6.45 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.79 [s, 1H, aromatic H *ortho* to $(CH_2OCH_2)_5$]. – IR (KBr): $\tilde{\nu}$ = 1645 cm^{-1} (νC=O). – $C_{27}H_{36}ClNaO_{13}$ (627.0): calcd. C 51.72, H 5.79, Cl 5.92; found C 51.50, H 5.91, Cl 5.65.

[26,29-Dimethoxy-2,5,8,11,14-pentaoxa[15](2,5)-p-benzoquinono[3]paracyclophane]calcium Bis(thiocyanate) (**6d**): Preparation by analogy with **6a** from 72.4 mg (0.14 mmol) of **4**, 20.3 mg (0.13 mmol) of calcium thiocyanate (very hygroscopic, therefore dried in vacuo at 70°C), 5 ml of acetone and 5 ml of diethyl ether. Yield 36.0 mg (42%, related to calcium thiocyanate) of red-purple crystals, which were dried in vacuo at 50°C, dec. >170°C. The crystals were suitable for X-ray analysis. – UV/Vis ($CHCl_3$): λ_{max} (ε) = 478 nm (1207), 299 (4535), 256 sh (11790), in CH_2Cl_2: λ_{CT} = 472 nm (ε = 1347). – ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 2.48 [br., 6H, $(CH_2)_3$], 3.72 [s, 3H, OCH_3 *ortho* to $(CH_2OCH_2)_5$], 3.79 [s, 3H, OCH_3 *ortho* to $(CH_2)_3$], 4.00 [mc, 14H, $OCH_2CH_2(OCH_2CH_2)_3O$], 4.15 [t, J = 4.4 Hz, 2H, OCH_2CH_2-$(OCH_2CH_2)_3O$], 4.50 br. (2H, allylic CH_2), 4.77 [s, 2H, benzylic CH_2], 6.06 [s, 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.25 [t, J = 1.7 Hz, 1H, benzoquinone H vicinal to $(CH_2OCH_2)_5$], 6.48 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.78 [s, 1H, aromatic H *ortho* to $(CH_2OCH_2)_5$]; at 328 K: δ = 2.21 br., 2.49 br., 2.69 br. [each 2H, $(CH_2)_3$], 3.73 [s, 3H, OCH_3 *ortho* to $(CH_2OCH_2)_5$], 3.79 [s, 3H, OCH_3*ortho* to $(CH_2)_3$], 3.92–4.00 [m, 14H, $OCH_2CH_2(OCH_2$-$CH_2)_3O$], 4.14 [t, J = 4.6 Hz, 2H, $OCH_2CH_2(OCH_2CH_2)_3O$], 4.51 (s, 2H, allylic CH_2), 4.78 (s, 2H, benzylic CH_2), 6.06 [s, 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.26 [t, J = 1.6 Hz, 1H, benzoquinone H vicinal to $(CH_2OCH_2)_5$], 6.48 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.78 [s, 1H, aromatic H *ortho* to $(CH_2OCH_2)_5$]; at 243 K: δ = 1.96 (mc, 1H, $CH_2CH_2CH_2$), 2.27 (mc, 1H, $CH_2CH_2CH_2$ at the benzoquinone), 2.38 (mc, 1H, $CH_2CH_2CH_2$ at the aromat), 2.52 (mc, 1H, $CH_2CH_2CH_2$), 2.78 (mc, 1H, $CH_2CH_2CH_2$ at the benzoquinone), 3.04 (mc, 1H, $CH_2CH_2CH_2$ at the aromat), 3.73 [s, 3H, OCH_3 *ortho* to $(CH_2OCH_2)_5$], 3.78–4.28 [m, 16H, $(OCH_2$-$CH_2O)_4$, 3.83 s, 3H, OCH_3 *ortho* to $(CH_2)_3$], 4.34, 4.63 (AB, J = 18 Hz, 2H, allylic CH_2), 4.69, 4.83 (AB, J = 14 Hz, 2H, benzylic CH_2), 4.96 (s, 2H, presumably coordinated H_2O), 6.08 [s, 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.24 [s, 1H, benzoquinone H vicinal to $(CH_2OCH_2)_5$], 6.48 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.83 [s, 1H, aromatic H *ortho* to $(CH_2OCH_2)_5$]; in CD_2Cl_2 at 243 K: δ = 1.95, 2.30, 2.38, 2.50, 2.71, 2.93 [each mc, 1H, $(CH_2)_3$], 3.60–4.30 [m, 22H, $O(CH_2CH_2O)_4$ + 2 OCH_3, 3.71, s, OCH_3 *ortho* to $(CH_2OCH_2)_5$, 3.77, s, OCH_3 *ortho* to $(CH_2)_3$], 4.40, 4.59 (AB, J = 18.2 Hz, 2H, allylic CH_2), 4.75, 4.78 (AB, J = 15.0 Hz, 2H, benzylic CH_2), 6.16 [s, 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.22 [s, 1H, benzoquinone H vicinal to $(CH_2OCH_2)_5$], 6.51 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.76 [s, 1H, aromatic H *ortho* to $(CH_2OCH_2)_5$]; assignment by H/H-COSY, NOED, and ROESY. – IR (KBr): $\tilde{\nu}$ = 2060, 2050 cm^{-1} (νNCS) 1650 (νC=O). – $C_{29}H_{36}CaN_2O_9S_2$ (660.8): calcd. C 52.71, H 5.49, N 4.24; found C 52.87, H 5.48, N 4.19.

[26,29-Dimethoxy-2,5,8,11,14-pentaoxa[15](2,5)-p-benzoquinono[3]paracyclophane]mercury(II) Bis(thiocyanate) (**6e**): A solution of 188 mg (0.37 mmol) of **4** and 118 mg (0.37 mmol) of $Hg(SCN)_2$ in 10 ml of methanol was refluxed for 5 min. The solution was concentrated in vacuo and the oily residue dissolved in 7 ml of hot ethyl acetate. After 48 h deposition of 132 mg (43%) of red crystals occurred, which were dried in vacuo at 50°C, mp 156°C, suitable for X-ray structure analysis. – UV/Vis ($CHCl_3$): λ_{max} (ε) = 475 nm (864), 293 (5585), 255 shoulder (14185). – ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 2.13 (br., 2H, $CH_2CH_2CH_2$), 2.47 (br., 2H, $CH_2CH_2CH_2$ at the benzoquinone), 2.72 (br., 2H, $CH_2CH_2CH_2$ at the aromat), 3.60–3.90 [m, 22H, $O(CH_2CH_2O)_4$ + 2 OCH_3, 3.71 s, OCH_3 *ortho* to $(CH_2OCH_2)_5$, 3.79 s, OCH_3 *ortho* to $(CH_2)_3$], 4.26 br. (2H, allylic CH_2), 4.51 br. (2H, benzylic CH_2), 6.23 [s, 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.49 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.56 [t, J = 1.2 Hz, 1H, benzoquinone H vicinal to $(CH_2OCH_2)_5$], 6.87 [s, 1H, aromatic H *ortho* to $(CH_2OCH_2)_5$]; at 323 K: δ = 2.10 (quint J = 6.1 Hz, 2H, $CH_2CH_2CH_2$), 2.45 (t, J = 6.3 Hz, 2H, $CH_2CH_2CH_2$ at the benzoquinone), 2.70 br. (2H, $CH_2CH_2CH_2$ at the aromat), 3.60–3.80 [m, 22H, $O(CH_2CH_2O)_4$ + 2 OCH_3], 4.27 (d, J = 2.1 Hz, 2H, allylic CH_2), 4.52 (s, 2H, benzylic CH_2), 6.26 [s, 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.51 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.58 [t, J = 1.2 Hz, 1H, benzoquinone H vicinal to $(CH_2OCH_2)_5$], 6.87 [s, 1H, aromatic H *ortho* to $(CH_2OCH_2)_5$]; at 223 K: δ = 1.92 [m, 1H, $(CH_2)_3$], 2.18 [t, J = 11 Hz, 1H, $(CH_2)_3$], 2.40 [t, J = 11 Hz, 1H, $(CH_2)_3$], 2.52 [m, 1H, $(CH_2)_3$], 2.84 [m, 1H, $(CH_2)_3$], 3.09 [m, 1H, $(CH_2)_3$], 3.50–4.10 [m, 22H, $O(CH_2CH_2O)_4$ + 2 OCH_3], 4.04, 4.53 (AB, J = 19 Hz, 2H, allylic CH_2), 4.31, 4.70 (AB, J = 16 Hz, 2H, benzylic CH_2), 6.14 [s, 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.51 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.53 [s, 1H, benzoquinone H vicinal to $(CH_2OCH_2)_5$], 6.83 [s, 1H, aromatic H *ortho* to $(CH_2OCH_2)_5$]; assignment by H/H-COSY and NOED. – IR (KBr): $\tilde{\nu}$ = 2140, 2120 cm^{-1} (νSCN), 1650 (νC=O). – $C_{29}H_{36}HgN_2O_9S_2$ (821.3): calcd. C 42.41, H 4.42, N 3.41, S 7.81; found C 42.46, H 4.22, N 3.32, S 7.27.

[29,32-Dimethoxy-2,5,8,11,14,17-hexaoxa[18](2,5)-p-benzoquinono[3]paracyclophane]barium Bis(thiocyanate) (**7**): A solution of 55 mg (0.1 mmol) of hexaoxa[18.3]paracyclophane quinhydrone **5**, 0.5 ml of triethyl orthoformate, and 24.9 mg (0.09 mmol) of $Ba(SCN)_2 \cdot 2\ H_2O$ in 5 ml of acetonitrile was refluxed for 5 min. By layering the cooled reaction solution with diethyl ether 45 mg [64%, related to $Ba(SCN)_2 \cdot 2\ H_2O$] of purple crystals deposited, mp 186°C (dec.). – UV/Vis ($CHCl_3$): λ_{max} (ε) = 472 nm (597), 297 (5100), 256 (14490) – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.15 (m, 2H, $CH_2CH_2CH_2$), 2.49 (m, 2H, $CH_2CH_2CH_2$ at the benzoquinone), 2.72 (m, 2H, $CH_2CH_2CH_2$ at the aromat), 3.76–4.02 [m, 26H, $O(CH_2CH_2O)_5$ + 2 OCH_3, 3.76 s, OCH_3 *ortho* to $(CH_2OCH_2)_6$, 3.79 s, OCH_3 *ortho* to $(CH_2)_3$], 4.51 (d, J = 1.2 Hz, 2H, allylic CH_2), 4.67 (s, 2H, benzylic CH_2), 5.99 ["t", 1H, benzoquinone H vicinal to $(CH_2)_3$], 6.29 ["t", 1H, benzoquinone H vicinal to $(CH_2OCH_2)_6$], 6.51 [s, 1H, aromatic H *ortho* to $(CH_2)_3$], 6.75 [s, 1H, aromatic H *ortho* to $(CH_2OCH_2)_6$]; assignment by H/H-COSY. – IR (KBr): $\tilde{\nu}$ = 2080, 2060 cm^{-1} (νNCS), 1650 (νC=O). – $C_{31}H_{40}BaN_2O_{10}S_2$ (802.1): calcd. C 46.42, H 5.03, N 3.49; found C 46.09, H 4.97, N 3.27.

Acetone instead of acetonitrile could also be used for the synthesis of the compound **7**. It was precipitated with diethyl ether as described above (yield 35%), decomposition of the crystals at 167°C. The purple crystals of the barium complex thereby obtained were suitable for X-ray analysis, although they still contained 1/2 mol of acetone. – $C_{31}H_{40}BaN_2O_{10}S_2$ + 1/2 CH_3COCH_3 (831.2): calcd. C 46.97, H 5.21, N 3.37; found C 46.86, H 5.14, N 3.16.

11,14,20,23-Tetramethoxy-2,5,8-trioxa[9.3]paracyclophane (**8a**, **8b**): A solution of 1.0 g (2.66 mmol) of 1,3-bis[4-(hydroxymethyl)-2,5-dimethoxyphenyl]propane (**15**) and 1.1 g (2.66 mmol) of diethylene glycol ditosylate in 100 ml of anhydrous THF was added dropwise during 3 h to a stirred suspension of 0.70 g (14.5 mmol) of 50% purified sodium hydride in 100 ml of anhydrous THF under reflux under nitrogen. The mixture was heated for a further 48 h. Excess sodium hydride was filtered, and the filtrate was concentrated in vacuo. The oily residue was shaken with dichloromethane/water until neutrality of the aqueous phase. The organic phase was dried with $MgSO_4$ and concentrated in vacuo. The yellowish oil (1.26 g) was chromatographed on a column of silica gel with ethyl acetate/cyclohexane (1:1). First fraction: 237 mg (20%) of colorless crystals, mp 80–95°C. After recrystallization from *n*-heptane pure **8a** was obtained as colorless prisms with mp 103–104°C. – ^{1}H NMR (500 MHz, $CDCl_3$, in solution equilibrium **8a** ⇌ **8b**): δ = 1.98–2.05 [m, 1H, $(CH_2)_3$ of **8a**], 2.36–2.42 [m, $(CH_2)_3$, 2H of **8a** and 4H of **8b**], 2.48–2.58 [m, 1H, $(CH_2)_3$ of **8a**], 2.98–3.04 [m, 2H, $(CH_2)_3$ of **8b**], 3.07–3.13 [m, 2H, $(CH_2)_3$ of **8a**], 3.50–3.80 [2m, each 8H, $O(CH_2$-$CH_2O)_2$ of **8a** and **8b**, 3.56, 2 OCH_3 of **8b** *ortho* to $(CH_2)_3$, 3.57, 2 OCH_3 of **8a** *ortho* to $(CH_2)_3$, 3.60, 2 OCH_3 of **8a** *ortho* to $(CH_2OCH_2)_3$, 3.70, 2 OCH_3 of **8b** *ortho* to $(CH_2OCH_2)_3$], 4.31, 4.64 (AB, J = 12.7 Hz, 4H, 2 benzylic CH_2 of **8a**), 4.27, 4.63 (AB, J = 12.1 Hz, 4H, 2 benzylic CH_2 of **8b**), 6.27 [s, 2H, aromatic H of **8a** *ortho* to $(CH_2)_3$], 6.41 [s, 2H, aromatic H of **8b** *ortho* to $(CH_2OCH_2)_3$], 6.53 [s, 2H, aromatic H of **8b** *ortho* to $(CH_2)_3$], 6.57 [s, 2H, aromatic H of **8a** *ortho* to $(CH_2OCH_2)_3$]. Assignment by H/H-COSY. In [D_6]DMSO, 304 K (80 MHz): δ = 6.34 (s, 2H, aromatic H of **8a**), 6.37 (s, 2H, aromatic H of **8b**), 6.51 (s, 2H, aromatic H of **8b**), 6.55 (s, 2H, aromatic H of **8a**); at 373 K: δ = 6.38, 6.46, 6.49, 6.55 (each s). – MS (200°C), *m/z*: 446 [M^+] (100%). – $C_{25}H_{34}O_7$ (446.6): calcd. C 67.24, H 7.67; found C 67.50, H 7.69.

Subsequent elution with ethyl acetate/cyclohexane (3:1) yielded as second fraction 135 mg (11%) of the dimer, mp 129°C (ethanol). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.82 [m, 4H, $(CH_2)_3$], 2.62 [t, J = 7 Hz, 8H, $(CH_2)_3$], 3.60–3.80 [m, 40H, OCH_3 + $O(CH_2CH_2O)_2$], 4.57 (s, 8H, benzylic CH_2), 6.67 (s, 4H, aromatic H), 6.92 (s, 4H, aromatic H). – MS (360–370°C), *m/z* (%): 891 [M^+ – 1] (30), 281 (100). – $C_{50}H_{68}O_{14}$ (893.1): calcd. C 67.24, H 7.67; found C 67.36, H 7.52.

14,17,23,26-Tetramethoxy-2,5,8,11-tetraoxa[12.3]paracyclophane (**9**): A solution of 4.0 g (8.0 mmol) of 1,3-bis[4-(bromomethyl)-2,5-dimethoxyphenyl]propane (**16**) in 500 ml of anyhdrous THF and a solution of 1.2 g (8.1 mmol) of triethylene glycol in 250 ml of anhydrous THF were added simultaneously dropwise over 7 h to a stirred, boiling suspension of 0.90 g (18.8 mmol) of 50% purified sodium hydride in 250 ml of anhydrous THF under nitrogen. The solution was refluxed for a further 15 h. After filtering off excess sodium hydride and concentration of the filtrate in vacuo the oily residue was dissolved in chloroform and the resulting solution washed with water until neutrality. The organic phase was dried with $MgSO_4$ and concentrated. The residual oil was chromatographed on a column of silica gel with ethyl acetate/cyclohexane (3:1) to give 1.37 g (35%) of colorless crystals with mp 87–89°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.15 [m, 2H, $(CH_2)_3$], 2.68 [t, J = 7 Hz, 4H, $(CH_2)_3$], 3.50–3.70 [m, 24H, 4 OCH_3 + $O(CH_2$-$CH_2O)_3$], 4.50 (s, 4H, benzylic CH_2), 6.44 (2H, aromatic H), 6.69 (2H, aromatic H). – MS (220–230°C), *m/z*: 490 [M^+] (100%). – $C_{27}H_{38}O_8$ (490.6): calcd. C 66.20, H 7.76; found C 66.21, H 8.00.

Compound **9** could also be obtained from **13** and triethylene glycol (yield 27%).

17,20,26,29-Tetramethoxy-2,5,8,11,14-pentaoxa[15.3]paracyclophane (**10**): The solutions of 3.86 g (7.7 mmol) of **16** in 500 ml of anyhdrous THF and 1.49 g (7.7 mmol) of tetraethylene glycol in 250 ml of anyhdrous THF were added dropwise during 10 h under argon simultaneously to a stirred and boiling suspension of 2.4 g (50 mmol) of 50% purified sodium hydride and ca. 50 mg of 18-crown-6 in 800 ml of anhydrous THF. The solution was

heated for a further 14 h. Excess sodium hydride was decomposed by adding a few drops of methanol. Then the mixture was concentrated in vacuo, the residue dissolved in chloroform and the resulting solution washed with a saturated sodium chloride solution until neutrality. The organic phase was dried with $MgSO_4$ and concentrated in vacuo. The oily residue was chromatographed on a column of silica gel with ethyl acetate/cyclohexane (3:1) to give 1.85 g (45%) of a colorless oil, which crystallized upon scratching with a glass rod, mp 85–87°C. – UV ($CHCl_3$): λ_{max} 294 nm (ε = 9780). – ^1H NMR (360 MHz $CDCl_3$): δ = 1.90 [quint, J = 7 Hz, 2H, $(CH_2)_3$], 2.61 [t, J = 7 Hz, 4H, $(CH_2)_3$], 3.50–3.60 [m, 16H, $O(CH_2CH_2O)_4$], 3.65 (s, 6H, 2 OCH_3), 3.74 (s, 6H, 2 OCH_3), 4.56 (s, 4H, benzylic CH_2), 6.61 (s, 2H, aromatic H), 6.87 (s, 2H, aromatic H). – MS (220°C), *m/z*: 534 [M^+] (100%). – $C_{29}H_{42}O_9$ (534.7); calcd. C 65.15, H 7.92; found C 64.96, H 7.97.

20,23,29,32-Tetramethoxy-2,5,8,11,14,17-hexaoxa[18.3]paracyclophane (**11**): A solution of 3.52 g (7.0 mmol) of **16** in 500 ml of anhydrous THF and a solution of 1.69 g (7.1 mmol) of pentaethylene glycol in 250 ml of anhydrous THF were added dropwise under argon during 10 h simultaneously to a stirred and boiling suspension of 4.8 g (100 mmol) of 50% purified sodium hydride and 100 mg of 18-crown-6 in 700 ml of anyhdrous THF. The solution was heated for a further 3 h. After decomposition of excess sodium hydride by the addition of some drops of methanol, 100 ml of water was added. The mixture was neutralized with 2 N HCl and shaken with dichloromethane. The organic phase was washed with water, dried with $MgSO_4$, and concentrated in vacuo. Purification of the yellowish oil on a column of silica gel with ethyl acetate/cyclohexane (3:1) yielded 1.56 g (39%) of colorless crystals, mp 67–69°C. – ^1H NMR (80 MHz, $CDCl_3$): δ = 1.85 [quint, J = 7 Hz, 2H, $(CH_2)_3$], 2.62 [t, J = 7 Hz, 4H, $(CH_2)_3$], 3.50–3.60 [m, 20H, $O(CH_2CH_2O)_5$], 3.71 (s, 6H, 2 OCH_3), 3.76 (s, 6H, 2 OCH_3), 4.57 (s, 4H, benzylic CH_2), 6.67 (s, 2H, aromatic H), 6.91 (s, 2H, aromatic H). – MS, *m/z*: 578 [M^+] (100%). – $C_{31}H_{46}O_{16}$ (578.7); calcd. C 64.34, H 8.01; found C 64.21, H 8.05.

1,3-Bis(2,5-dimethoxyphenyl)-2-propen-1-one[7], *Modified Preparation:* A suspension of 9.5 g (97.5%, 0.17 mol) of sodium ethoxide in 100 ml of anhydrous methanol was added under nitrogen during 5 min to a stirred solution of 20.6 g (0.12 mol) of 97% 2,5 dimethoxybenzaldehyde and 21.8 g (0.12 mol) of 99% 2,5-dimethoxyacetophenone in 160 ml of anhydrous methanol at 40°C. The mixture was stirred at 40°C for a further 2 h and then allowed to stand at room temp. for 12 h. The yellow-orange reaction mixture was poured into 1 l of cold water and neutralized with concentrated hydrochlorid acid. The precipitated yellow oil was shaken three times with 250 ml of ether and the ether solution four times with 50 ml of a 20% aqueous $Na_2S_2O_5$ solution, subsequently twice with 100 ml of water, then concentrated in vacuo and purified over a short column of Al_2O_3. After removal of the solvent a yellow oil in almost quantitative yield was obtained. The crude product was used for the further reaction. The oil could be chromatographed on Al_2O_3 with $CHCl_3/CCl_4$ (3:2). – Instead of using chromatography the compound could also be purified by heating to 180°C at 0.01 Torr. During this process more volatile compounds were distilled. – ^1H NMR (360 MHz, $CDCl_3$): δ = 3.78, 3.79, 3.82, 3.84 (each s, 3H, OCH_3), 6.83–7.12 (m, 6H, aromatic H), 7.41, 7.93 (AB, J = 16 Hz, 2H, olefinic H). – IR ($CHCl_3$): $\tilde{\nu}$ = 1650 cm^{-1} (νC=O). – $C_{19}H_{20}O_5$ (328.4): calcd. C 69.50, H 6.14; found C 69.50, H 6.22.

1,3-Bis(2,5-dimethoxyphenyl)propan-1-one[7], *Modified Preparation:* A solution of 39.6 g (0.12 mol) of 1,3-bis(2,5-dimethoxyphenyl)-2-propen-1-one in 450 ml of ethyl acetate was hydrogenated with 1.5 g of 5% Pd/C in a glass vessel at normal pressure. After 2 h the catalyst was filtered, the filtrate concentrated in vacuo, and the residue recrystallized from methanol to yield 29.9 g (75%) of colorless crystals, mp 69°C (ref.[7] 79–80°C, this mp is by 10°C too high). – ^1H NMR (80 MHz, $CDCl_3$): δ = 3.85–3.40 (m, 4H, CH_2CH_2), 3.70–3.90 (m, 12H, OCH_3), 6.70–7.30 (m, 6H, aromatic H). – IR (KBr): $\tilde{\nu}$ = 1670 cm^{-1} (νC=O). – $C_{19}H_{22}O_5$ (330.4): calcd. C 69.07, H 6.71; found C 69.40, H 6.90.

1,3-Bis(2,5-dimethoxyphenyl)propane (**12**)[7,15], *Modified Preparation:* A solution of 20.0 g (60.7 mmol) of 1,3-bis(2,5-dimethoxyphenyl)propan-1-one and 0.80 g of *p*-toluenesulfonic acid hydrate in 400 ml of methanol was hydrogenated by shaking with 0.5 g of 10% Pd/C at normal pressure. After 3 h the catalyst was filtered and the filtrate concentrated in vacuo. The crude product was recrystallized from ethanol to give 17 g (89%) of colorless crystals, mp 62°C. (61–62°C[7]). – ^1H NMR (360 MHz, $CDCl_3$): δ = 1.88 (quint, J = 7.5 Hz, 2H, $CH_2CH_2CH_2$), 2.65 (t, J = 8 Hz, 4H, $CH_2CH_2CH_2$), 3.74 (s, 6H, OCH_3), 3.76 (s, 6H, OCH_3), 6.65–6.76 (m, 6H, aromatic H). – MS (140–150°C), *m/z*: 316 [M^+] (100%). – $C_{19}H_{24}O_4$ (316.4): calcd. C 72.13, H 7.65; found C 72.27, H 7.87.

For the preparation of such quantities of **12** the two-step hydrogenation of 1,3-bis(2,5-dimethoxyphenyl)-2-propen-1-one is preferred to a one-step procedure.

1,3-Bis[4-(chloromethyl)-2,5-dimethoxyphenyl]propane (**13**): The reaction should be carried out in a very efficient exhaustor, since bis(chloromethyl) ether might develop. HCl gas was passed into a solution of 12 ml of 35% (140 mmol) of aqueous formaldehyde and 6 ml of conc. HCl in 25 ml of dioxane cooled to 5–10°C. The temp. rose to 55–60°C. To this mixture 9.48 g (30 mmol) of **12** was added in portions in such a way that the temp. remained at 55–60°C. After completion of the reaction the addition of HCl was interrupted. The mixture was allowed to stand for 1 h, then treated with 120 ml of ice/water and 30 ml of diethyl ether. The aqueous phase was shaken twice with 20 ml of diethyl ether, the combined ether phases were washed with cold water until neutrality. After drying of the solution with $MgSO_4$ and concentration in vacuo, the residue was recrystallized from ethyl acetate to give 11.25 g (91%) of colorless crystals, mp 172–173°C. – ^1H NMR (80 MHz, $CDCl_3$): δ = 1.90 (mc, 2 H, $CH_2CH_2CH_2$), 2.67 (t, J = 8 Hz, 4 H, $CH_2CH_2CH_2$), 3.78 (s, 6H, OCH_3), 3.82 (s, 6H, OCH_3), 4.64 (s, 4H, benzylic CH_2), 6.72 (s, 2H, aromatic H), 6.84 (s, 2H, aromatic H). – MS (240–250°C), *m/z*: 412 [M^+ for ^{35}Cl] (100%). – $C_{21}H_{26}Cl_2O$ (413.3): calcd. C 61.02, H 6.34, Cl 17.15; found C 61.28, H 6.53, Cl 16.90

1,3-Bis([4-(acetoxymethyl)-2,5-dimethoxyphenyl]propane (**14**): A suspension of 2.0 g (4.85 mmol) of **13** and 2.0 g (24.4 mol) of sodium acetate in 200 ml of acetic acid was heated with stirring for 2 h to 100°C. First, a clear solution developed, then sodium chloride precipitated. After cooling to room temp. the mixture was filtered. The filtrate was concentrated in vacuo to 60 ml, treated with water and shaken with ethyl acetate. The organic phase was first washed with a $NaHCO_3$ solution and then with water. After drying with $MgSO_4$ it was concentrated in vacuo to give 1.8 g (80%) of colorless crystals, mp 120°C (from cyclohexane or methanol), TLC with CH_2Cl_2, R_f = 0.5. – ^1H NMR (80 MHz, $CDCl_3$): δ = 1.90 (mc, 2H, $CH_2CH_2CH_2$), 2.69 (t, J = 7.5 Hz, 4H, $CH_2CH_2CH_2$), 3.79 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 5.13 (s, 4H, benzylic CH_2), 6.73 (s, 2H, aromatic H), 6.84 (s, 2H, aromatic H). – IR (KBr): $\tilde{\nu}$ = 1725 cm^{-1} (νC=O). – MS (250°C), *m/z*: 460 [M^+] (100%). – $C_{25}H_{32}O_8$ (460.5): calcd. C 65.20, H 7.00; found C 65.50, H 7.25.

1,3-Bis[4-(hydroxymethyl)-2,5-dimethoxyphenyl]propane (**15**): A suspension of 1.78 g (3.87 mmol) of **14** and 75 ml of 20% NaOH in 230 ml of methanol was refluxed for 7 h. A clear solution developed. After concentration of the reaction solution in vacuo the residue was shaken with 300 ml of acetone. The acetone solution was dried with K_2CO_3 and concentrated in vacuo. The yellowish solid product was recrystallized from toluene to give 1.0 g (69%) of colorless crystals, mp 167–168°C. – ^1H NMR (80 MHz, $CDCl_3$): δ = 1.86 (mc, 2H, $CH_2CH_2CH_2$), 2.27 (t, J = 7 Hz, 2H, OH), 2.68 (t, J = 7.5 Hz, 4H, $CH_2CH_2CH_2$), 3.79 (s, 6H, OCH_3), 3.81 (s, 6H, OCH_3), 4.65 (d, J = 7 Hz, 4H, benzylic CH_2), 6.71 (s, 2H, aromatic H), 6.81 (s, 2H, aromatic H); upon H/D exchange with D_2O the triplet at δ = 2.27 disappeared; in [D_6]DMSO: δ = 1.82 (mc, 2H, $CH_2CH_2CH_2$), 2.57 (t, J = 7.5 Hz, 4H, $CH_2CH_2CH_2$), 3.71 (s, 12H, OCH_3), 4.29 (br., 2H, OH), 4.46 (s, 4H, benzylic CH_2), 6.72 (s, 2H, aromatic H), 6.97 (s, 2H, aromatic H); upon H/D exchange with D_2O the signal at δ = 4.29 disappeared. – IR (KBr): $\tilde{\nu}$ = 3240 br., 3130 cm^{-1} (νOH). – MS (260°C), *m/z*: 376 [M^+] (100%). – $C_{21}H_{28}O_6$ (376.5): calcd. C 67.00, H 7.50, OCH_3 32.97; found C 67.10, H 7.18, OCH_3 32.59.

1,3-Bis[4-(bromomethyl)-2,5-dimethoxyphenyl]propane (**16**): 30 ml of 33% HBr in acetic acid was added dropwise to a suspension of 15.0 g (47.4 mmol) of **12** and 4.5 g (150 mmol) of paraformaldehyde in 150 ml of tetrachloromethane. First, a clear solution developed, then a white precipitate formed. After 1 h 30 ml of a saturated sodium hydrogen carbonate solution was added to decompose any bis(bromomethyl) ether. The precipitate was filtered and washed successively with 30 ml of a saturated $NaHCO_3$ solution, 50 ml of water, and 50 ml of tetrachloromethane. After recrystallization from chloroform 20.05 g (85%) of colorless crystals with mp 190–191°C was obtained. – ^1H NMR (360 MHz, $CDCl_3$): δ = 1.86 (quint, J = 7.5 Hz, 2H, $CH_2CH_2CH_2$), 2.65 (t, J = 7.8 Hz, 4H, $CH_2CH_2CH_2$), 3.77 (s, 6H, OCH_3), 3.84 (s, 6H, OCH_3), 4.56 (s, 4H, benzylic CH_2), 6.70 (s, 2H, aromatic H), 6.81 (s, 2H, aromatic H). – MS (300°C), *m/z* (%): 500 [M^+, for ^{79}Br] (12), 177 (100). – $C_{21}H_{26}Br_2O_4$ (502.2): calcd. C 50.22, H 5.22, Br 31.82; found C 50.24, H 4.92, Br 31.32.

1,3-Bis(2,5-dimethoxy-4-methylphenyl)propane (**17**): A solution of 2.94 g (5.85 mmol) of **16** in 80 ml of anyhdrous THF was added dropwise at room temp. under nitrogen to a stirred suspension of 1.1 g (29 mmol) of $LiAlH_4$ in 150 ml of anyhdrous THF. Then the mixture was stirred under reflux for a further 22 h. In order to decompose excess $LiAlH_4$, first 2 ml of ethyl acetate, then 2 ml of water were added to the mixture. After neutralization with 2 N H_2SO_4 the solution was concentrated in vacuo. The residue was shaken with chloroform/water and dried with $MgSO_4$. After removal of the solvent in vacuo and recrystallization of the crude product from methanol 1.58 g (86%) of colorless crystals with mp 151°C was obtained (subl. at 130°C). – ^1H NMR (360 MHz, $CDCl_3$): δ = 1.87 (quint, J = 7.5 Hz, 2H, $CH_2CH_2CH_2$), 2.19 (s, 6H, CH_3 at the aromat), 2.64 (t, J = 7.5 Hz, 4H, $CH_2CH_2CH_2$), 3.76 (s, 6H, OCH_3), 3.77 (s, 6H, OCH_3), 6.66 (s, 4H, aromatic H). – MS (140–150°C), *m/z*: 344 (100%). – $C_{21}H_{28}O_4$ (344.45): calcd. C 73.23, H 8.19, OCH_3 36.05; found C 73.25, H 8.00, OCH_3 36.29.

1,3-Bis[2,5-dimethoxy-4-(methoxymethyl)phenyl]propane (**18**): A suspension of 0.50 g (9.2 mmol) of sodium methoxide in 20 ml of methanol was added dropwise to a stirred solution of 0.95 g (1.9 mmol) of **16** in 50 ml of methanol. Stirring under reflux was continued for a further 3 h. The mixture was poured onto 100 ml of ice/water, neutralized with 2 N HCl and shaken with diethyl ether. The ether solution was washed with water, dried with $MgSO_4$, and concentrated in vacuo. Recrystallization of the residue from methanol yielded 655 mg (85%) of colorless crystals, mp 88°C. – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.87 (quint, *J* = 7.7 Hz, 2H, $CH_2CH_2CH_2$), 2.66 (t, *J* = 7.7 Hz, 4H, $CH_2CH_2CH_2$), 3.42 (s, 6H, CH_2OCH_3), 3.78 (s, 6H, OCH_3 at the aromat), 3.79 (s, 6H, OCH_3 at the aromat), 4.47 (s, 4H, benzylic CH_2), 6.70 (s, 2H, aromatic H), 6.90 (s, 2H, aromatic H). – MS (250–260°C), *m/z*: 404 [M^+] (100%). – $C_{23}H_{32}O_6$ (404.5): calcd C 68.29, H 7.97; found C 68.58, H 7.69.

1,3-Bis[4-(ethoxymethyl)-2,5-dimethoxyphenyl]propane (**19**): A solution of 0.60 g (1.19 mmol) of **16** and 0.30 g (2.97 mmol) of triethylamine in 200 ml of ethanol was allowed to stand at room temp. for 24 h. The solvent was removed in vacuo, the residue shaken with dichloromethane/water, and the organic phase dried with $MgSO_4$ and concentrated in vacuo. The crude material (0.41 g) was recrystallized from *n*-heptane to give 0.38 g (74%) of colorless crystals, mp 95–96°C. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7 Hz, 6H, OCH_2CH_3), 1.88 (mc, 2H, $CH_2CH_2CH_2$), 2.65 (t, *J* = 8 Hz, 4H, $CH_2CH_2CH_2$), 3.57 (q, *J* = 7 Hz, 4H, OCH_2CH_3), 3.78 (s, 6H, OCH_3), 3.80 (s, 6H, OCH_3), 4.52 (s, 4H, benzylic CH_2), 6.70 (s, 2H, aromatic H), 6.91 (s, 2H, aromatic H). – MS (220°C), *m/z*: 432 [M^+] (100%). – $C_{25}H_{36}O_6$ (432.6): calcd. C 69.42, H 8.39; found C 70.31, H 8.38; found C 67.96, H 8.43.

2,5,8,11,14-Pentaoxa[15.3](2,5)-p-benzoquinonophane (**20**). – *Method A:* A solution of 1.64 g (3.0 mmol) of diammonium hexanitratocerate in 7 ml of water was rapidly added dropwise to a solution of 0.32 g (0.6 mmol) of tetramethoxy[15.3]paracyclophane **10** and 0.55 g (3.0 mmol) of 2,6-pyridinedicarboxylic acid *N*-oxide in 15 ml of acetonitrile. The reaction solution turned first red, then orange-yellow. After 10 min this solution was shaken twice with 50 ml of dichloromethane/water (1:1), the organic phase washed with water, dried with $MgSO_4$, and concentrated in vacuo. After chromatography of the residue on a column of silica gel with ethyl acetate/cyclohexane (3:1) an orange-red oil was obtained, which crystallized upon the addition of a little diethyl ether to give 86 mg (30%) of yellow crystals, mp 94–95°C. – UV ($CHCl_3$): λ_{max} (ε) = 412 nm (83), 254 (30485). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.85 (quint, *J* = 7 Hz, 2H, $CH_2CH_2CH_2$), 2.43 (t, *J* = 6 Hz, 4H, $CH_2CH_2CH_2$), 3.66–3.72 [m, 16H, $O(CH_2CH_2O)_4$], 4.40 (d, *J* = 2 Hz, 4H, allylic CH_2), 6.47 [s, 2H, benzoquinone H vicinal to $(CH_2)_3$], 6.84 [t, *J* = 2 Hz, 2H, benzoquinone H, vicinal to $(CH_2OCH_2)_5$]. – IR (KBr): $\tilde{\nu}$ = 1660 (νC=O). – MS (>400°C), *m/z* (%): 476 [M^+ + 2] (<1), 474 [M^+] (<1), 89 (100). – $C_{25}H_{30}O_9$ (474.5): calcd. C 63.28, H 6.37; found C 63.45, H 6.36.

Method B: 1.37 g (2.5 mmol) of diammonium hexanitratocerate in 10 ml of water was added dropwise over 5 min at 0°C to a stirred solution of 492 mg (0.98 mmol) of dimethoxypentaoxa[15.3]paracyclophane quinhydrone **4** and 457 mg (2.5 mmol) of 2,6-pyridinedicarboxylic acid *N*-oxide in 15 ml of acetonitrile. The formerly red-colored suspension turned yellow. After stirring of the mixture for a further 20 min at room temp. it was shaken with 100 ml of dichloromethane/water (1:1). The aqueous phase was shaken with further 50 ml of dichloromethane. The combined organic phases were washed with 100 ml of water, dried with $MgSO_4$, and concentrated in vacuo. After chromatography of the residue in analogy to method A 185 mg (40%) of **20** was obtained.

2-[3-(2,5-Dimethoxyphenyl)propyl]-p-benzoquinone (**21**): A solution of 1.3 g (2.37 mmol) of diammonium hexanitratocerate in 15 ml of water was added dropwise to a stirred solution of 0.30 g (0.95 mmol) of **12** in 60 ml of acetonitrile. During this addition the solution turned red. After 30 min the mixture was shaken with dichloromethane/water (1:1). The organic phase was dried with $MgSO_4$ and concentrated in vacuo to give 0.26 g of an orange oil. After chromatograpy of this oil on a column of silica gel with cyclohexane/ethyl acetate (2:1) 0.21 g (77%) of an orange-red oil was obtained. (According to ref.[15] the oil should crystallize to give orange-red crystals with mp 164–167°C after standing for a few months.) – UV/Vis ($CHCl_3$): λ_{max} (ε) = 445 nm sh (80), 292 (4380), 248 (21100). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.55–2.0 (m, 2H, $CH_2CH_2CH_2$), 2.3–2.75 (m, 4H, $CH_2CH_2CH_2$), 3.73 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3); 6.5–6.75 (m, 6H, benzoquinone H and aromatic H). – IR (Film): $\tilde{\nu}$ = 1650 cm^{-1} (νC=O). – MS (110°C), *m/z*: 286 [M^+ (100%). – $C_{17}H_{18}O_4$ (286.3): calcd. C 71.31, H 6.34, OCH_3 21.68; found C 70.90, H 6.23, OCH_3 21.93.

2-[3-(2,5-Dimethoxy-4-methylphenyl)propyl]-5-methyl-p-benzoquinone (**22**): A solution of 1.08 g (1.97 mmol) of diammonium hexanitratocerate in 10 ml of water was added dropwise at room temp. to a stirred solution of 0.27 g (0.79 mmol) of **17** in 50 ml of acetonitrile. During the addition the solution turned yellow-orange. After 30 min the mixture was shaken twice with dichloromethane/water (1:1). The combined organic phases were washed with water, dried with $MgSO_4$, and concentrated in vacuo. After chromatography of the residue on a column of silica gel with ethyl acetate/cyclohexane (1:3) 156 mg (63%) of orange crystals with mp 89–91°C (*n*-heptane) was obtained. – UV/Vis ($CHCl_3$): λ_{max} (ε) = 440 nm sh (99), 292 (4360), 260 sh (20500), 254 (22100). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.65–1.95 (m, 2H, $CH_2CH_2CH_2$), 2.0 (d, *J* = 2 Hz, 3H, CH_3 at the benzoquinone), 2.17 (s, 3H, CH_3 at the aromat), 2.32–2.77 (m, 4H, $CH_2CH_2CH_2$), 3.75 and 3.76 (s, 3H each, OCH_3), 6.50–6.70 (m, 4H, benzoquinone H and aromatic H). – IR (KBr): $\tilde{\nu}$ = 1635 cm^{-1} (νC=O). – MS (150–160°C), *m/z* (%): 314 [M^+] (52), 152 (100). – $C_{19}H_{22}O_4$ (314.4): calcd. C 72.59, H 7.05, OCH_3 19.74; found C 72.52, H 7.42, OCH_3 19.16.

2-{3-[2,5-Dimethoxy-4-(methoxymethyl)phenyl]propyl}-5-(methoxymethyl)-p-benzoquinone (**23**): A solution of 1.59 g (2.90 mmol) of diammonium hexanitratocerate in 40 ml of water was added dropwise at room temp. to a stirred solution of 5.58 mg (1.38 mmol) of **18** in 110 ml of acetonitrile. After stirring for 1 h the orange-yellow solution was shaken twice with 30 ml of dichloromethane/water (1:1). The combined organic phases were dried with $MgSO_4$ and concentrated in vacuo. Chromatography of the residue on a column of silica gel with ethyl acetate/cyclohexane (1:3) gave 330 mg (64%) of yellow-orange crystals, mp 75–78°C (*n*-hexane). – UV/Vis ($CHCl_3$): λ_{max} (ε) = 445 nm sh (92), 293 (5570), 253 (19734). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 1.81 (quint, *J* = 7.5 Hz, 2H, $CH_2CH_2CH_2$), 2.46 (dt, J_d = 1, J_t = 6.9 Hz, 2H, $CH_2CH_2CH_2$ at the benzoquinone), 2.64 (t, *J* = 7.6 Hz, 2H, $CH_2CH_2CH_2$ at the aromat), 3.42, 3.45 (s, 3H each, CH_2OCH_3), 3.79 (s, 6H, OCH_3 at the aromat), 4.28 (d, *J* = 2 Hz, 2H, allylic CH_2), 4.45 (s, 2H, benzylic CH_2), 6.55 (t, *J* = 1.3 Hz, 1H, benzoquinone H), 6.66 (s, 1H, aromatic H), 6.74 (t, *J* = 2 Hz, 1H, benzoquinone H), 6.88 (s, 1H, aromatic H). – IR (KBr): $\tilde{\nu}$ = 1655, 1645 cm^{-1} (νC=O). – MS (180–190°C), *m/z*: 374 [M^+] (100%). – $C_{21}H_{26}O_6$ (374.4): calcd. C 67.36, H 7.00; found C 67.51, H 7.26.

2-(Ethoxymethyl)-5-{3-[4-(ethoxymethyl)-2,5-dimethoxyphenyl]propyl}-p-benzoquinone (**24**): A solution of 0.95 g (1.74 mmol) of diammonium hexanitratocerate in 20 ml of water was added dropwise at room temp. to a stirred solution of 0.30 g (0.69 mmol) of **19** in 40 ml of acetonitrile. The solution turned yellow-orange. After 40 min the mixture was shaken with dichloromethane/water (1:1). The yellow organic phase was dried with $MgSO_4$ and concentrated in vacuo. Chromatography of the yellow-orange, oily residue on a column of silica gel with cyclohexane/ethyl acetate (3:1) gave 125 mg (45%) of orange needles, mp 69°C (*n*-heptane). – UV/Vis ($CHCl_3$): λ_{max} (ε) = 445 nm sh (100), 292 (5950), 254 (20500). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7 Hz, 6H, OCH_2CH_3), 1.65–2.05 (m, 2H, $CH_2CH_2CH_2$), 2.60 (mc, 4H, $CH_2CH_2CH_2$), 3.61 (2 q, *J* = 7 Hz, 4H, OCH_2CH_3), 3.80 (s, 6H, OCH_3 at the aromat), 4.34 (d, *J* = 2 Hz, 2H, allylic CH_2), 4.53 (s, 2H, benzylic CH_2), 6.57 (t, *J* = 1 Hz, 1H, benzoquinone H), 6.68 (s, 1H, aromatic H), 6.79 (t, *J* = 2 Hz, 1H, benzoquinone H), 6.93 (s, 1H, aromatic H). – IR (KBr): $\tilde{\nu}$ = 1625 cm^{-1} br. (νC=O). – MS (180–190°C), *m/z*: 402 [M^+] (100%). – $C_{23}H_{30}O_6$ (402.5): calcd. C 68.64, H 7.51; found C 68.29, H 7.52.

2-[9-(2,5-Dimethoxyphenyl)-2,5,8-trioxanonyl]-p-benzoquinone (**25**): A solution of 2.0 g (3.65 mmol) of diammonium hexanitratocerate in 20 ml of water was added dropwise at room temp. to a stirred solution of 0.61 g (1.50 mmol) of **28** in 70 ml of acetonitrile. During the addition the solution turned red. After 30 min the mixture was shaken with dichloromethane/water (1:1). The organic phase was dried with $MgSO_4$, concentrated in vacuo and the red, oily residue chromatographed on a column of silica gel with ethyl acetate/cyclohexane (1:1). The first yellow-brown zone was **25**, yield 0.42 g (74%) of orange crystals, mp 67–69°C (*n*-heptane). – UV/Vis: λ_{max} (ε) = 437 nm (47), 293 (4080), 247 (20750). – ^{1}H NMR (360 MHz, $CDCl_3$): δ = 3.68–3.74 [m, 8H, $O(CH_2CH_2O)_2$], 3.76, 3.78 (each s, 3H, OCH_3), 4.41 (d, *J* = 2.2 Hz, 2H, allylic CH_2), 4.59 (s, 1H, benzylic CH_2), 6.71, 6.72 (2H, benzoquinone H), 6.76, 6.77 (2H, aromatic H), 6.87 (m, 1H, benzoquinone H), 7.00 (m, 1H, aromatic H). – IR (KBr): $\tilde{\nu}$ = 1655 cm^{-1}, sh, 1645 (νC=O). – MS (220–230°C), *m/z* (%): 376 [M^+] (80), 151 (100). – $C_{20}H_{24}O_7$ (376.4): calcd. C 63.82, H 6.43; found C 63.83, H 6.63.

The compounds **26**, **27**, **33**, and **34** were synthesized analogously.

2-[12-(2,5-Dimethoxyphenyl)-2,5,8,11-tetraoxadodecyl]-p-benzoquinone (**26**): From **29** with diammonium hexanitratocerate; highly viscous orange oil (TLC, R_f = 0.3). – UV/Vis ($CHCl_3$): λ_{max} (ε) = 440 nm sh (60), 295 sh (4770), 284 (5290), 245 sh (23000). – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 3.60–3.70 [m, 12H, $O(CH_2CH_2O)_3$], 3.76 (s, 6H, OCH_3), 4.40 (d, *J* = 2 Hz, 2H, allylic CH_2), 4.57 (s, 2H, benzylic CH_2), 6.70, 6.71 (2H, benzoquinone H), 6.75, 6.77 (2H, aromatic H), 6.86 (m, 1H, benzoquinone H), 7.0 (m, 1H, aromatic H). – IR (film): $\tilde{\nu}$ = 1655 cm^{-1}, br. (νC=O). – MS (260°C), *m/z* (%): 420 [M^+] (17), 151 (100). – $C_{22}H_{28}O_8$ (420.5): calcd. C 62.85, H 6.71; found C 63.04, H 6.76.

Table 4. Crystallographic data and refinement parameters

	6d	6e	7	8a	20
Formula	$C_{27}H_{36}O_9 \cdot Ca(SCN)_2$	$C_{27}H_{36}O_9 \cdot Hg(SCN)_2$	$C_{29}H_{40}O_{10} \cdot Ba(SCN)_2 \cdot 0.5\ CH_3COCH_3$	$C_{25}H_{34}O_7$	$C_{25}H_{30}O_9$
Mol. mass	660.8	821.3	831.2	446.6	474.5
Cryst. descript.	red needles	red needles	red prisms	colorless prisms	orange needles
Cryst. size [mm]	0.05 x 0.1 x 0.3	0.08 x 0.08 x 0.3	0.25 x 0.30 x 0.35	0.15 x 0.15 x 0.25	0.1 x 0.1 x 0.25
Cryst. system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)
a [pm]	798.0(1)	1975.5(3)	2151.3(2)	890.7(2)	950.7(2)
b [pm]	1176.6(2)	811.8(1)	1447.4(1)	2138.4(3)	2452.6(4)
c [pm]	1753.5(3)	2087.9(3)	2451.7(3)	1228.7(2)	1120.8(2)
α [°]	88.97(1)	-	-	-	-
β [°]	80.28(1)	104.24(2)	90.00(2)	96.86(2)	114.30(2)
γ [°]	78.71(1)	-	-	-	-
Z	2	4	8	4	4
D_{calc}	1.380	1.681	1.447	1.276	1.323
F_{000} [e]	696	1632	3392	960	1008
μ(Mo-K_α) [cm^{-1}]	3.69	49.15[a]	11.97[a]	0.863	0.940
Unique reflns measured up to sin Θ/λ [nm^{-1}]	5594 6.0	6347 6.2	7457 6.2	4075 6.0	4186 6.0
Observed reflns with $I \geq 3.0\ \sigma(I)$	3218	4157	5475	2497	1878
Struct. solution	direct methods (MULTAN)	heavy-atom method (PATTERSON)	heavy-atom method (PATTERSON)	direct methods (MULTAN)	direct methods (MULTAN)
R	0.039	0.035	0.034	0.059	0.049

[a] Empirical absorption correction (ψ-scans) performed.

2-[15-(2,5-Dimethoxy-4-methylphenyl)-2,5,8,11,14-pentaoxapentadecyl]-5-methyl-p-benzoquinone (**27**): From **31** with diammonium hexanitratocerate; orange-yellow oil. – UV/Vis ($CHCl_3$): λ_{max} (ε) = 440 nm sh (42), 292 (4000), 253 (24273). – ^1H NMR (80 MHz, $CDCl_3$): δ = 2.02 (d, J = 2 Hz, 3H, CH_3 at the benzoquinone), 2.19 (s, 3H, CH_3 at the aromat), 3.60–3.70 [m, 16H, $O(CH_2CH_2O)_4$], 3.78, 3.75 (each s, 3H, OCH_3), 4.38 (d, 2 Hz, 2H, allylic CH_2), 4.56 (s, 2H, benzylic CH_2), 6.56 (q, J = 2 Hz, 1H, benzoquinone H), 6.68 (s, 1H, aromatic H), 6.83 (t, J = 2 Hz, 1H, benzoquinone H), 6.91 (s, 1H, aromatic H). – MS (300°C), *m/z* (%): 492 [M^+] (14), 165 (100). – $C_{26}H_{36}O_9$ (492.6): calcd. C 63.40, H 7.37; found C 63.21, H 7.53.

2,5,8,11,14-Pentaoxa[15](2',5'-dimethoxy-2,5-diphenoquinonophane) (**33**): From **30** with diammonium hexanitratocerate; red prisms, mp 103–105°C (ref.[11] 116°C). – UV/Vis ($CHCl_3$): λ_{max} (ε) = 464 nm (1100), 360 (865), 298 (7620). – ^1H NMR identical with that in ref.[11]. – MS (230–240°C), *m/z*: 462 [M^+] (100%). – $C_{24}H_{30}O_9$ (462.5): calcd. C 62.33, H 6.54; found C 62.25, H 6.95.

2,5,8,11,14,17-Hexaoxa[18](2',5'-dimethoxy-2,5-diphenoquinonophane) (**34**): From **32** with diammonium hexanitratocerate; red crystals, mp 119–122°C (ref.[11] 124–126°C). – UV/Vis ($CHCl_3$): λ_{max} (ε) = 467 nm (1173), 298 (10477), 242 (20954). – ^1H NMR; identical with that in ref.[11]. – MS (260–270°C), *m/z*: 506 [M^+] (100%). – $C_{26}H_{34}O_{10}$ (506.6): calcd. C 61.65, H 6.77; found C 61.55, H 6.95.

1,9-Bis(2,5-dimethoxyphenyl)-2,5,8-tioxanonane (**28**): A solution of 1.5 g (15 mmol) of diethylene glycol in 10 ml of anhydrous tetrahydrofuran was added dropwise at room temp. to a stirred suspension of 2.0 g (42 mmol) of 50% sodium hydride and 0.5 g of NaI in 20 of ml anhydrous tetrahydrofuran. The mixture was refluxed for 1 h. After cooling to room temp. 5.57 g (30 mmol) of 2,5-dimethoxybenzyl chloride in 20 ml of anhydrous tetrahydrofuran was added, and the mixture was stirred under reflux for 24 h. After filtration the filtrate was concentrated and the residue chromatographed on a column of silica gel with dichloromethane/methanol (95:5) to give as crude material 5.0 g (82%) of a yellowish oil. (For the oxidative demethylation it was used without further purification.) – ^1H NMR (80 MHz, $CDCl_3$): δ = 3.69 [s, 8H, $O(CH_2CH_2O)_2$], 3.75 (s, 12H, OCH_3), 4.59 (d, J = 1 Hz, 4H, benzylic CH_2), 6.75, 6.77 (4H, aromatic H), 7.01 (t, J = 1 Hz, 2H, aromatic H). – MS (150–160°C), *m/z* (%): 406 [M^+] (46), 255 (100). The oil was distilled in a kugelrohr apparatus. – $C_{22}H_{30}O_7$ (406.5): calcd. C 65.01, H 7.44; found C 65.63, H 7.08.

The homologous compounds **29**–**32** were prepared analogously and used in the oxidative demethylation reaction directly as raw materials.

1,12-Bis(2,5-dimethoxyphenyl)-2,5,8,11-tetraoxadodecane (**29**): From 2,5-dimethoxybenzyl chloride and triethylene glycol; yellowish oil. – ^1H NMR (80 MHz, $CDCl_3$): δ = 3.67 [s, 12H, $O(CH_2CH_2O)_3$], 3.73 (s, 12H, OCH_3), 4.57 (s, 4H, benzylic CH_2), 6.75, 6.77 (4H, aromatic H), 7.01 ("t", 2H, aromatic H). – MS (200°C), *m/z* (%): 450 [M^+] (5), 151 (100). – $C_{24}H_{34}O_8$ (450.2): calcd. C 63.98, H 7.61; found C 64.20, H 7.64.

1,15-Bis(2,5-dimethoxyphenyl)-2,5,8,11,14-pentaoxapentadecane (**30**): From 2,5-dimethoxybenzyl chloride and tetraethylene glycol; yellowish oil. – ^1H NMR (360 MHz, $CDCl_3$): δ = 3.66, 3.67 [16H, $O(CH_2CH_2O)_4$], 3.76 (s, 12H, OCH_3), 4.57 (s, 4H, benzylic CH_2), 6.75 (d, 4H, aromatic H), 7.00 ("t", 2H, aromatic H). – MS (260–270°C), *m/z* (%): 494 [M^+] (16), 151 (100). – $C_{26}H_{38}O_9$ (494.6): calcd. C 63.14, H 7.74; found C 63.22, 7.92.

1,15-Bis(2,5-dimethoxy-4-methylphenyl)-2,5,8,11,14-pentaoxapentadecane (**31**): From 2,5-dimethoxy-4-methylbenzyl chloride and tetraethylene glycol; yellowish oil. – 1H NMR (80 MHz, $CDCl_3$): δ = 2.21 (s, 6H, CH_3), 3.66 [s, 16H, $O(CH_2CH_2O)_4$], 3.75, 3.79 (s, 6H each, OCH_3), 4.57 (s, 4H, benzylic CH_2), 6.67 (s, 2H, aromatic H), 6.91 (s, 2H, aromatic H). – MS (360–370°C), *m/z* (%): 522 [M^+] (4), 164 (100). – $C_{28}H_{42}O_9$ (522.6): calcd. C 64.35, H 8.10; found C 64.32, H 8.07.

1,18-Bis(2,5-dimethoxyphenyl)-2,5,8,11,14,17-hexaoxaoctadecane (**32**): From 2,5-dimethoxybenzyl chloride pentaethylene glycol; yellowish oil. – ^1H NMR (80 MHz, $CDCl_3$): δ = 3.60–3.70 [m, 20H, $O(CH_2CH_2O)_5$], 3.74 (s, 12H, OCH_3), 4.56 (s, 4H, benzylic CH_2), 6.73, 6.75 (4H, aromatic H), 7.00 (m, 2H, aromatic H). – MS (300°C), *m/z* (%): 538 [M^+] (15), 151 (100). – $C_{28}H_{42}O_{10}$ (538.6): calcd. C 62.44, H 7.86; found C 62.15, H 7.58.

X-Ray Structural Analysis of **6d**, **6e**, **7**, **8a**, *and* **20** (Table 4): Suitable crystals of **6d** and **7** were obtained by layering an acetone solution with ether. Crystals of **6e** were obtained from ethyl acetate, crystals of **8a** from *n*-heptane, and crystals of **20** from ether. – For X-ray crystal structure determinations the intensity data were collected by means of a four-circle diffractometer (Enraf-Nonius CAD 4) by using a graphite-monochromated Mo-K_α (λ = 0.07107 nm) radiation and by applying ω–2δ scan technique. Refinements by full-matrix least-squares technique using anisotropic temperature factors for all non-hydrogen atoms and isotropic ones for hydrogen atoms. For further details of the X-ray data of the crystal structures see ref.[16].

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