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Electron Donor-Acceptor Compounds, XXXVI[1)]

Quinones and Quinhydrones of the [2.2]- and [3.3]Metaparacyclophane Series

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The isomeric quinhydrones **1** and **2** as well as the bis(quinone) **6** of the [2.2]metaparacyclophane series were synthesized. Precursor of these products was the tetramethoxy[2.2]metaparacyclophane **3** which was prepared via **4** and **5**. X-ray structure analyses of **1**, **3** and **6** are discussed with regard to the steric strain in these molecules and the donor-acceptor orientation in **1**. Charge-transfer absorptions of **1** and **2** are reported as well as circular dichroism of **1** which was separated into enantiomers. – Following an analogous route the isomeric quinhydrones **13** and **14** as well as the bis(quinone) **15** of the [3.3]metaparacyclophane series were prepared. The difference in steric strain of the [3.3]- in comparison to the [2.2]metaparacyclophane series is discussed on the basis of an X-ray structure analysis of **13**. Charge-transfer absorptions of **13** and **14** are reported.

Elektron-Donor-Acceptor-Verbindungen, XXXVI[1)]

Chinone und Chinhydrone der [2.2]- und [3.3]Metaparacyclophan-Reihen

Die isomeren Chinhydrone **1** und **2** sowie das Bis(chinon) **6** der [2.2]Metaparacyclophan-Reihe wurden synthetisiert. Vorstufe dieser Verbindungen war das Tetramethoxy[2.2]metaparacyclophan **3**, das über **4** und **5** dargestellt wurde. Röntgen-Strukturanalysen von **1**, **3** und **6** werden im Hinblick auf die sterische Spannung dieser Moleküle und die Donor-Acceptor-Orientierung in **1** diskutiert. Charge-transfer-Absorptionen von **1** und **2** werden ebenso behandelt wie der Circulardichroismus von **1**, das in Enantiomere getrennt werden konnte. – Auf analogem Wege wurden die isomeren Chinhydrone **13** und **14** sowie das Bis(chinon) **15** der [3.3]Metaparacyclophan-Reihe dargestellt. Der Unterschied in der sterischen Spannung zwischen den [3.3]- und [2.2]-Metaparacyclophan-Reihen wird auf der Grundlage der Röntgen-Strukturanalyse von **13** diskutiert. Charge-transfer-Absorptionen von **13** und **14** werden angegeben.

In a recent publication of *Tashiro* et al.[2)] the introductory statement is made that "[2.2]metaparacyclophane quinones have not been synthesized previously". This statement is incorrect since already in 1979 we reported on the synthesis, X-ray structure analysis and spectroscopic properties of quinones and quinhydrones of the [2.2]metaparacyclophane series[3)]. Since our results, even as documented at that time, are more complete than the present results of the aforementioned authors are, we give here a full account of our work together with additional results from the [3.3]metaparacyclophane series.

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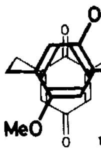
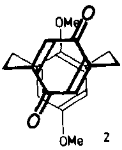
With intramolecular quinhydrones of the paracyclophane[4] and metacyclophane[5] series we studied extensively the dependence of charge-transfer (CT) absorptions on orientation and distance of the donor and acceptor units. It was quite obvious that we included into these studies metaparacyclophane quinhydrones which, in a well-defined, fixed geometry, contain the donor-acceptor pair in an arrangement different from that of the previously investigated series. Furthermore, we expected [2.2]metaparacyclophane quinhydrones to exist in two structural isomers like **1** and **2** the comparison of which was again relevant with regard to the different donor-acceptor orientation.

Synthesis of Quinhydrones of the [2.2]Metaparacyclophane Series

For the synthesis of **1** and **2** the 5,8,12,15-tetramethoxy[2.2]metaparacyclophane **3** was considered as key intermediate which should be accessible via the corresponding dithia[3.3]metaparacyclophane **4** and the disulfone **5** derived therefrom and from which **1** and **2** should be available by partial demethylation followed by oxidation.



1



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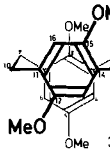

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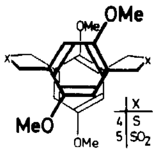


	X
4	S
5	SO_2

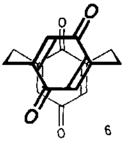
4 was obtained by cyclisation of 1,4-bis(mercaptomethyl)-2,5-dimethoxybenzene and 1,3-bis(bromomethyl)-2,5-dimethoxybenzene (potassium carbonate, boiling tetrahydrofuran/dimethylformamide, 1:1; high dilution; 43% yield; m.p. 163.5°C). **4** of which analytical and spectroscopic data are given in the Experimental Part was oxidized to the disulfone **5** (60% hydrogen peroxide in water/acetic acid/dichloromethane; 3 d, 20°C; 89%). Vapour-phase pyrolysis[6] at 520°C/0.005 Torr yielded the sterically extremely crowded **3** in the surprisingly high yield of 80%. In addition to **3** small yields (1.5 – 2% each) of **1** and **2** were separated chromatographically from the pyrolysis products (see below). **3** was also obtained by photolysis of **5** in toluene suspension (yields up to 70%, variable).

For **3** (m.p. 112 – 113°C) the low molecular symmetry is reflected by the ^{1}H NMR absorptions (80 MHz, $CDCl_3$): The methylene bridges give rise to ABCD multiplets (δ = 2.0 – 3.5, m, 8H); the four methoxy groups show four singlets (3H) at δ = 3.20, 3.35, 3.72, and 3.85. As compared to the absorptions of 2,5-dimethoxy-1,4-xylene and 2,5-dimethoxy-1,3-xylene, resp., two of these signals are considerably highfield-shifted. From the steric situation as determined by X-ray structure analysis (see below) it is seen that one methoxy group of each of the two aromatic rings (8- and 12-CH_3O) is in the shielding region of the neighbouring aromatic system; this assignment is also supported by NOE results. Of the aromatic protons those of the *para*-bridged ring absorb as singlets at δ = 5.50 and 6.56, the difference between these signals again being in accordance with the transanular anisotropy effects to be predicted; the two protons of the *meta*-bridged ring which in relation to the opposite ring are in a more similar position absorb at δ = 6.33 („s“, 2H; d at 360 MHz). Further analytical and spectroscopic results supporting structure **3** are presented in the Experimental Part. The data of an

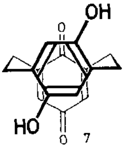
X-ray structure analysis which due to the extreme steric situation in **3** was of special interest are given below.

Demethylation experiments on **3** were expected to be complicated by the very different steric hindrance of the four methoxy groups. Complete demethylation of **3** which after oxidation yielded the bis(quinone) **6** was only achieved by treating **3** with boron tribromide (dichloromethane, 45 min, 20°C; 70% yield). Analytical and spectroscopic data of **6** (m. p. 197°C) agree well with the data given recently by *Tashiro* et al.[2] who prepared **6** along a different route. Results of an X-ray structure analysis of **6** are given below.

On attempts to cleave the methoxy groups in **3** with methylmagnesium iodide (1 h, 160°C) no **6** was obtained after oxidation. Instead by partial demethylation and subsequent oxidation **1** was obtained in dark rubin-red crystals (m. p. 142°C) in 30% yield. Isomer **2**, however, was not isolated from these reactions. Obviously, the demethylation of the methoxy groups on the *meta*-bridged ring is preferred over the corresponding reaction on the *para*-bridged ring. Models show that this result is difficult to understand in terms of simple steric hindrance. On the other hand, demethylation of one of the two methoxy groups on the *meta*-bridged ring (8-CH_3O) results in the strongest release of sterical strain, and thus the demethylation of this ring might be favored. The results of the X-ray structure analysis of **3** support this conclusion.



6



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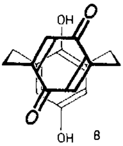

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Partial catalytic hydrogenation of bis(quinone) **6** (1 equ. H_2, palladium oxide, ethyl acetate) led immediately to a dark-red solution indicating a quinhydrone redox state. From the solution a dark-red product was obtained for which the mass spectrum shows the predicted addition of two hydrogens (m/z = 270). ^1H NMR spectra are, however, in accordance with neither **7** or **8** but with a mixture of the two isomers which are difficult to separate. *Tashiro* et al.[2] obviously also did not obtain pure **7** or **8** by partial hydrogenation of **6**; they managed, however, to prepare one isomer, presumably **8**, by partial oxidation of the tetrahydroxy[2.2]metaparacyclophane derived from **6** by complete reduction; there is no report about the second isomer.

Since the synthetic procedures mentioned above provided us with the pair of isomeric quinhydrones **1** and **2** we concentrated on the structural assignment and the spectroscopic comparison of these isomers with regard to CT interaction. The structure determination of **1** and **2** was first based on mass spectra and ^1H NMR data. For **1** and **2** the molecular ions form the base peaks of the spectra [MS: **1**: m/z = 298 (100%, M^+), 164 (18), 134 (17) a.o.; **2**: m/z = 298 (100%, M^+), 151 (49), 149 (18), 121 (15) a.o.]. As found for other [2.2]phanes with at least one *para*-bridged dimethoxy-substituted ring as well, for **1** the major fragmentation leads to the dimethoxy-stabilized *para*-quinodimethane fragment ion (m/z = 164); the peak of second highest intensity (m/z = 134), however, does not belong to the complementary fragment $C_8H_6O_2$ of the same fragmentation but according to high-resolution mass spectra and meta-stable peaks is due to a fragment $C_9H_{10}O$ which is formed from the fragment $m/z = 164$ by loss of CH_3O. Without going into further details with regard to the fragmentation of **2** it can be stated that the complete lack of a fragment $m/z = 164$ excludes a partial structure of a dimethoxy-substituted *para*-bridged ring. Due to the instability of dimethoxy-substituted *meta*-quinodimethane-like structures alternative fragmentations leading to $C_9H_{11}O_2$ ($m/z = 151$) and $C_9H_9O_2$ ($m/z = 149$) become predominant.

This assignment derived for **1** and **2** is further supported by ^1H NMR [**1**: $\delta = 2.0-4.1$ (m, 8H), 3.65 (s, 3H), 3.87 (s, 3H), 6.12 and 6.28 (AB, $J = 2.75$ Hz, 2H), 6.18 (s, 1H), 6.51 (s, 1H); **2**: $\delta = 2.14$ (s, 3H), 2.4-4.9 (m, 8H), 3.75 (s, 3H), 6.15 and 6.20 (AB, $J \approx 2.75$ Hz, 2H), 6.25 (s, 1H), 6.60 (s, 1H); 80 MHz, $CDCl_3$]. Models for **2** show that one of the two methoxy groups due to the orientation and very short distance should be affected strongly by the anisotropic effect of the neighbouring quinone ring. In fact, for the compound marked as **2** an extremely highfield-shifted methoxy signal with $\Delta\delta = 1.61$ ppm relative to the second methoxy group of this molecule is observed. For **1**, on the other hand, the two methoxy groups are expected to be in rather similar chemical environments. As shown below this spectroscopic structural assignment of **1** and **2** has been confirmed by an X-ray structure analysis of **1**.

Molecular Structure of 1, 3, and 6[7]

X-Ray Structure Analysis: Crystal and data collection parameters for **1**, **3**, and **6** are listed in Table 1. Intensity data were collected using graphite-monochromated Mo-K_α radiation and applying $\Theta/2\Theta$ technique. The structures were solved by conventional methods (MULTAN) and were refined by full-matrix least-squares technique using anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms. Atomic coordinates and thermal parameters for non-hydrogen atoms of **1**, **3**, and **6** are given in Tables 2, 3, and 4, respectively. For numbering of atoms which follow the "phane rules" see Figures 1 A, 2 A, and 3 A.

Table 1. Crystal and Data Collection Parameters for **1**, **3**, and **6**

Compound	**1**	**3**	**6**
Formula	$C_{18}H_{18}O_4$	$C_{20}H_{24}O_4$	$C_{16}H_{12}O_4$
Molecular mass	298.3	328.4	268.3
a [pm]	769.8(1)	1613.1(2)	2469.8(3)
b [pm]	820.5(1)	830.4(1)	907.7(2)
c [pm]	2402.5(5)	1354.0(2)	1106.5(2)
β [°]	–	111.33(2)	92.39(2)
Space group	$P2_12_12_1$	$P2_1/c$	$C2/c$
Z	4	4	8
D_x [gcm^{-3}]	1.31	1.29	1.44
Max. sin. Θ/λ [nm^{-1}]	6.83	6.72	6.62
No. of reflections measured	2346	4121	3015
No. of reflections with $I > 1.96\sigma(I)$	1910	3330	2429
R	0.036	0.040	0.041

Table 2. Atomic Coordinates and Thermal Parameters $U_{equ.}$ (in pm^2) of Non-Hydrogen Atoms of **1** (Numbers in Parentheses are Estimated Standard Deviations in the Last Quoted Digits)

Atom	x	y	z	Uequ.	Atom	x	y	z	Uequ.
C(1)	0.1400(2)	0.2233(2)	0.38073(8)	533(6)	C(12)	0.3749(2)	-0.1608(2)	0.41980(7)	472(5)
C(2)	0.3061(3)	0.3145(2)	0.35524(8)	615(6)	C(13)	0.2701(2)	-0.0251(2)	0.42525(6)	437(5)
C(3)	0.4772(2)	0.2403(2)	0.37226(7)	486(5)	C(14)	0.1860(2)	0.0429(2)	0.37994(7)	463(5)
C(4)	0.5673(2)	0.2014(2)	0.41761(7)	529(5)	C(15)	0.1824(2)	-0.0460(2)	0.33027(7)	523(5)
C(5)	0.7109(2)	0.1006(3)	0.43584(7)	541(5)	C(16)	0.2916(3)	-0.1785(2)	0.32424(7)	543(5)
C(6)	0.7580(2)	0.0340(2)	0.40757(7)	542(6)	C(12")	0.4657(3)	-0.1455(3)	0.51494(8)	732(7)
C(7)	0.6753(2)	-0.0115(2)	0.36141(7)	486(5)	C(15")	0.0058(3)	-0.0579(3)	0.23541(9)	840(8)
C(8)	0.5524(2)	0.1093(2)	0.33605(7)	500(5)	O(5')	0.0053(2)	0.2320(2)	0.47598(6)	023(5)
C(9)	0.6998(3)	-0.1743(3)	0.33240(8)	625(6)	O(8')	0.5215(2)	0.1073(2)	0.28640(5)	728(5)
C(10)	0.5726(3)	-0.3075(2)	0.35353(8)	588(6)	O(12')	0.4758(2)	-0.2228(2)	0.46234(5)	634(4)
C(11)	0.4012(2)	-0.2277(2)	0.36702(7)	500(5)	O(15')	0.0057(2)	0.0216(2)	0.28796(5)	712(5)

Table 3. Atomic Coordinates and Thermal Parameters $U_{equ.}$ (in pm^2) of Non-Hydrogen Atoms of **3** (Numbers in Parentheses are Estimated Standard Deviations in the Last Quoted Digits)

Atom	x	y	z	Uequ.	Atom	x	y	z	Uequ.
C(1)	0.15202(7)	0.2920(1)	0.13197(9)	496(4)	C(13)	0.26105(7)	0.2368(1)	0.31482(8)	461(3)
C(2)	0.15441(7)	0.1494(1)	0.05748(8)	473(4)	C(14)	0.17431(7)	0.2308(1)	0.24351(8)	440(3)
C(3)	0.23090(6)	0.0361(1)	0.11258(7)	399(3)	C(15)	0.11557(7)	0.1281(1)	0.26728(8)	441(3)
C(4)	0.31695(7)	0.0762(1)	0.12305(8)	426(3)	C(16)	0.14912(7)	0.0099(2)	0.34395(8)	474(3)
C(5)	0.38950(6)	-0.0061(1)	0.19330(8)	411(3)	C(5")	0.54768(7)	-0.0199(2)	0.27852(9)	570(4)
C(6)	0.37622(7)	-0.1223(1)	0.25931(8)	421(3)	C(8")	0.09875(8)	-0.2576(2)	0.0670(1)	585(4)
C(7)	0.29055(6)	-0.1663(1)	0.25052(8)	407(3)	C(12")	0.44162(8)	0.2331(2)	0.4408(1)	713(5)
C(8)	0.21878(6)	-0.0967(1)	0.17005(7)	390(3)	C(15")	-0.03217(7)	0.0207(2)	0.2117(1)	613(4)
C(9)	0.27606(7)	-0.2697(1)	0.33565(9)	509(4)	O(5')	0.47204(5)	0.0418(1)	0.19531(6)	540(3)
C(10)	0.28004(7)	-0.1700(2)	0.43502(8)	552(4)	O(8')	0.13287(4)	-0.15002(9)	0.15401(5)	473(2)
C(11)	0.24000(7)	-0.0054(2)	0.39951(7)	479(3)	O(12')	0.38260(5)	0.1147(1)	0.46020(6)	634(3)
C(12)	0.29475(7)	0.1220(2)	0.39353(8)	400(4)	O(15')	0.02772(5)	0.1385(1)	0.20873(6)	542(3)

Table 4. Atomic Coordinates and Thermal Parameters $U_{equ.}$ (in pm^2) of Non-Hydrogen Atoms of **6** (Numbers in Parentheses are Estimated Standard Deviations in the Last Quoted Digits)

Atom	x	y	z	Uequ.	Atom	x	y	z	Uequ.
C(1)	0.35192(6)	0.5412(1)	0.2475(1)	441(4)	C(11)	0.30781(4)	0.0934(1)	0.2942(1)	333(3)
C(2)	0.41018(5)	0.4927(1)	0.2145(1)	483(4)	C(12)	0.30642(4)	0.1925(1)	0.4020(1)	333(3)
C(3)	0.43025(5)	0.3642(1)	0.2902(1)	386(3)	C(13)	0.31403(5)	0.3509(1)	0.3808(1)	355(3)
C(4)	0.45403(5)	0.3767(1)	0.3994(1)	440(4)	C(14)	0.31962(5)	0.4047(1)	0.2697(1)	346(3)
C(5)	0.46681(5)	0.2479(2)	0.4769(1)	453(4)	C(15)	0.30177(5)	0.3120(1)	0.1642(1)	384(3)
C(6)	0.44306(5)	0.1044(1)	0.4369(1)	448(4)	C(16)	0.29722(5)	0.1521(1)	0.1840(1)	381(3)
C(7)	0.41968(5)	0.0054(1)	0.3280(1)	403(3)	O(5')	0.49220(4)	0.2606(1)	0.57342(8)	637(3)
C(8)	0.42099(5)	0.2117(1)	0.2411(1)	391(3)	O(8')	0.41626(4)	0.1923(1)	0.13215(8)	559(3)
C(9)	0.39103(5)	-0.0555(1)	0.2866(1)	491(4)	O(12")	0.30404(4)	0.1434(1)	0.50431(7)	495(3)
C(10)	0.33037(5)	-0.0588(1)	0.3132(1)	421(4)	O(15')	0.29652(4)	0.3652(1)	0.06295(8)	599(3)

Molecular Structure of **1**: For the structure analysis of **1** rubin-red orthorhombic prisms have been used in which separated enantiomers crystallize in the chiral space group $P2_12_12_1$. From **1** there exist at least two crystal modifications of the racemate the structures of which were not solved [A: monoclinic, $P2_1/c$, a = 788.1(1), b = 2420.3(4), c = 868.0(2) pm, β = 113.94(2)°, Z = 4; B: monoclinic, $P2_1/c$, a = 2320.0(5), b = 844.3(2), c = 1603.9(4) pm, β = 109.17(2)°, Z = 8].

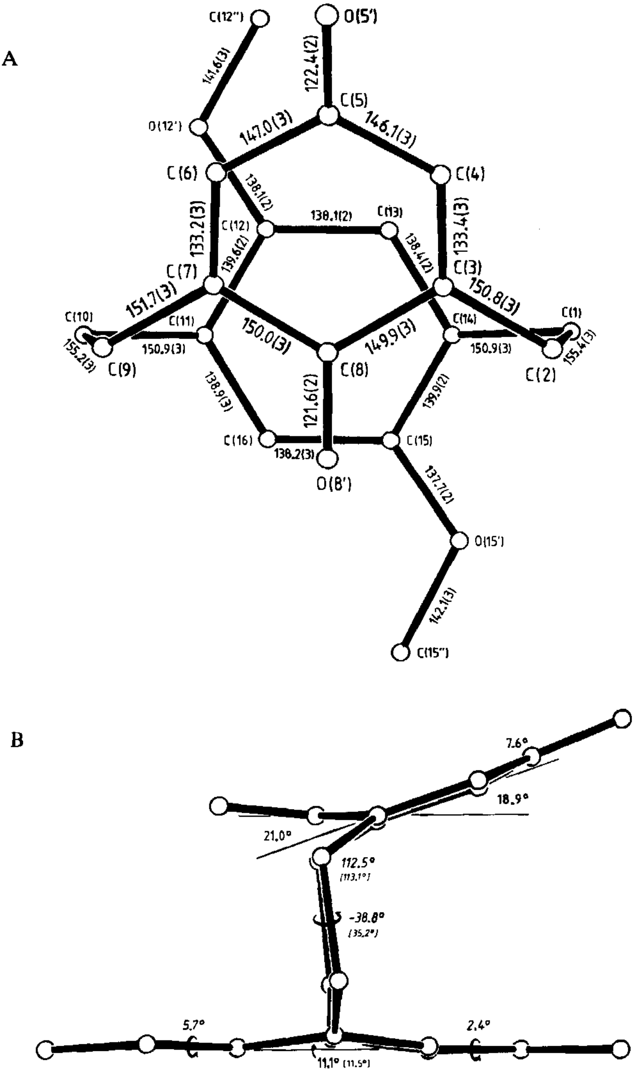


Figure 1. Molecular Structure of **1** in a Top-View Perpendicular to the *para*-Bridged Ring (A) and in a Side-View (B)

Figure 1A shows a top-view of **1** perpendicular to the plane of the *para*-bridged unit; in Figure 1B a side-view of the molecule is drawn. As is generally found for strained cyclophane quinhydrones, the *meta*-bridged quinone unit exhibits a much stronger deformation from planarity than the aromatic part of the molecule. In the quinone ring the carbonyl-containing triangle C(3) – C(8) – C(7) is bent away from the neighbouring aromatic ring by forming an angle of 21° with the central quinone plane C(3) – C(4) – C(6) – C(7). Nevertheless, the carbonyl carbon C(8) is closely above the centre of the aromatic ring with a transanular distance of only 287 pm. The quinone ring is deformed to a boat conformation the less crowded side, however, being only slightly distorted from planarity [angle C(4) – C(5) – C(6)/C(3) – C(4) – C(6) – C(7): 7.6°]. The *para*-bridged aromatic ring of **1** shows a typical paracyclophane-like boat-deformation with angles of 11.5 and 11.1° between the triangles C(16) – C(11) – C(12) and C(13) – C(14) – C(15), respectively, with the boat base C(12) – C(13) – C(15) – C(16). The methoxy groups are nearly coplanar to the aromatic ring. As an important point it should be mentioned that the quinoid ring and the aromatic ring, as defined by their boat bases, are inclined to each other by an angle of 18.9°. This inclination leads to a rather wide range of transanular distances between the quinoid and aromatic rings: Apart from the short distances between the bridge-heads [C(3) ··· C(14): 277, C(7) ··· C(11): 276 pm] in the overcrowded part there are rather short distances between C(8) ··· C(16) (311), C(8) ··· C(15) (312), O(8′) ··· C(16) (308), and O(8′) ··· C(15) (308 pm) whereas, for example, the transanular distance C(4) ··· C(13) is 341 pm.

Bond lengths of **1** are presented in Figure 1 A. Bond angles and some selected torsional angles are listed in Table 5.

Table 5. Bond Angles of **1** (Estimated Standard Deviations are Given in Parentheses in Units of the Last Quoted Digits)

C(2) - C(1) - C(14)	108.4(2)	C(8) - C(7) - C(9)	118.3(2)	C(12) - C(13) - C(14)	121.6(2)
C(1) - C(2) - C(3)	112.5(2)	C(3) - C(8) - C(7)	118.0(2)	C(1) - C(14) - C(13)	118.5(2)
C(2) - C(3) - C(4)	125.0(2)	C(3) - C(8) - O(8′)	120.2(2)	C(1) - C(14) - C(15)	121.2(2)
C(2) - C(3) - C(8)	118.0(2)	C(7) - C(8) - O(8′)	120.9(2)	C(13) - C(14) - C(15)	118.0(2)
C(4) - C(3) - C(8)	117.0(2)	C(7) - C(9) - C(10)	113.1(2)	C(14) - C(15) - C(16)	119.2(2)
C(3) - C(4) - C(5)	121.9(2)	C(9) - C(10) - C(11)	108.4(2)	C(14) - C(15) - O(15′)	115.5(2)
C(4) - C(5) - C(6)	118.3(2)	C(10) - C(11) - C(12)	119.5(2)	C(16) - C(15) - O(15′)	124.7(2)
C(4) - C(5) - O(5′)	121.2(2)	C(10) - C(11) - C(16)	119.9(2)	C(11) - C(16) - C(15)	121.3(2)
C(6) - C(5) - O(5′)	120.3(2)	C(12) - C(11) - C(16)	118.0(2)	C(12) - O(12′) - C(12″)	117.7(2)
C(5) - C(6) - C(7)	121.9(2)	C(11) - C(12) - C(13)	119.2(2)	C(15) - O(15′) - C(15″)	118.1(2)
C(6) - C(7) - C(8)	117.0(2)	C(11) - C(12) - O(12′)	116.5(2)		
C(6) - C(7) - C(9)	124.6(2)	C(13) - C(12) - O(12′)	123.7(2)		

Molecular Structure of **3**: In contrast to **1**, **3** is a regular [2.2]metaparacyclophane with two aromatic rings in which, however, of the four methoxy substituents the one on C(8) increases considerably the steric strain of the molecule. With exception of the distances between the bridge-head carbons [C(3) ··· C(14): 278.7(2); C(7) ··· C(11): 277.8(2) pm] the shortest transanular distances are from the methoxy oxygen O(8′) to C(15) and C(16) with 282.1(2) and 284.2(2) pm, respectively. In this context, it is interesting that the C(8) – O(8′) bond in comparison with the other three methoxy groups is significantly elongated; it should be mentioned, however, that this is also the only methoxy group which is arranged almost perpendicular to the aromatic ring. Both the *meta*- and the *para*-bridged aromatic rings show a boat-type deformation: In the *para*-bridged ring both C(11) and C(14) deviate for 13° from the central plane of this ring; in the *meta*-bridged ring it is, of course, the sterically crowded C(8) which deviates most (11°) from the ring plane leaving C(8) still in a rather short transanular distance (289 pm) above the plane of the neighbouring *para*-bridged ring. The two aromatic rings are inclined to each other with an angle of 13°. Figure 2A shows a top-view of **3** perpendicular to the plane of the *para*-bridged ring; in Figure 2B a side-view of **3** is presented.

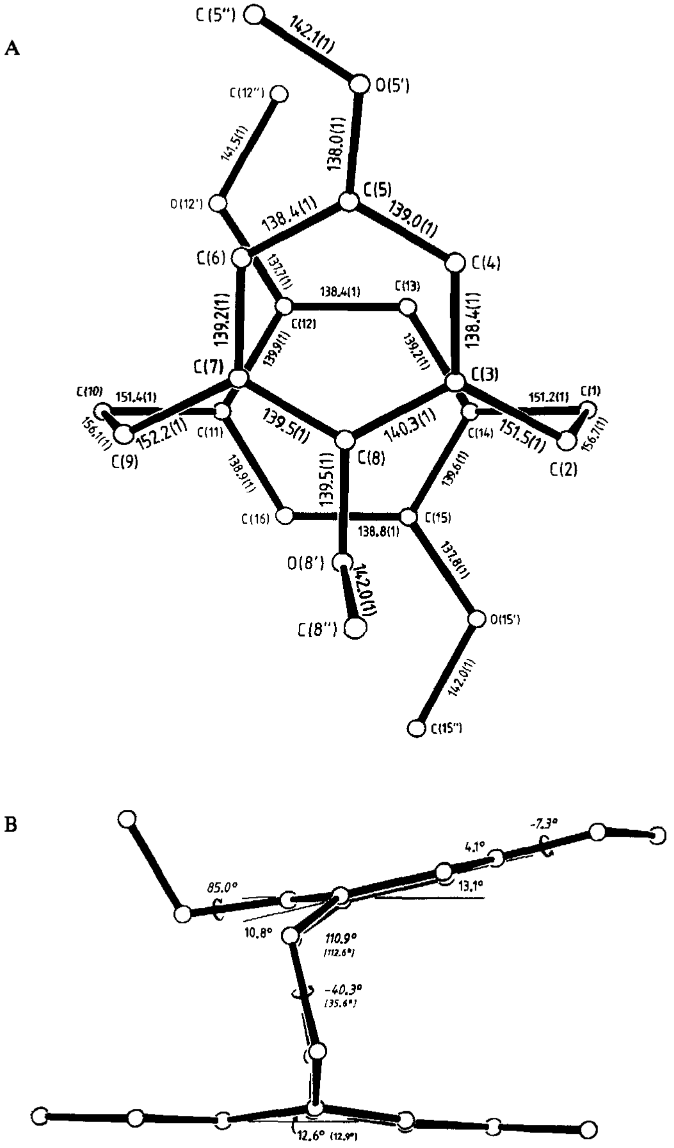


Figure 2. Molecular Structure of **3** in a Top-View Perpendicular to the *para*-Bridged Ring (A) and in a Side-View (B)

Table 6. Bond Angles of **3** (Estimated Standard Deviations are Given in Parentheses in Units of the Last Quoted Digits)

C(2) – C(1) – C(14)	109.4(1)	C(8) – C(7) – C(9)	120.9(1)	C(12) – C(13) – C(14)	121.2(1)
C(1) – C(2) – C(3)	110.9(1)	C(3) – C(8) – C(7)	121.8(1)	C(1) – C(14) – C(13)	119.1(1)
C(2) – C(3) – C(4)	120.5(1)	C(3) – C(8) – O(8')	119.6(1)	C(1) – C(14) – C(15)	120.7(1)
C(2) – C(3) – C(8)	120.6(1)	C(7) – C(8) – O(8')	119.8(1)	C(13) – C(14) – C(15)	117.7(1)
C(4) – C(3) – C(8)	118.8(1)	C(7) – C(9) – C(10)	112.6(1)	C(14) – C(15) – C(16)	119.5(1)
C(3) – C(4) – C(5)	121.8(1)	C(9) – C(10) – C(11)	109.1(1)	C(14) – C(15) – O(15')	115.7(1)
C(4) – C(5) – C(6)	119.7(1)	C(10) – C(11) – C(12)	119.7(1)	C(16) – C(15) – O(15')	124.2(1)
C(4) – C(5) – O(5')	116.0(1)	C(10) – C(11) – C(16)	119.9(1)	C(11) – C(16) – C(15)	121.2(1)
C(6) – C(5) – O(5')	124.3(1)	C(12) – C(11) – C(16)	117.6(1)	C(5) – O(5') – C(5")	117.1(1)
C(5) – C(6) – C(7)	120.7(1)	C(11) – C(12) – C(13)	119.5(1)	C(8) – O(8') – C(8")	113.1(1)
C(6) – C(7) – C(8)	118.3(1)	C(11) – C(12) – O(12')	116.7(1)	C(12) – O(12') – C(12")	118.1(1)
C(6) – C(7) – C(9)	120.3(1)	C(13) – C(12) – O(12')	123.4(1)	C(15) – O(15') – C(15")	117.7(1)

Bond lengths of **3** are shown in Figure 2 A. Bonds angles and some selected torsional angles are listed in Tab. 6.

Molecular Structure of **6**: The X-ray structure analysis of **6** completes the trilogy of [2.2]metaparacyclophanes in which (a) both six-menbered rings are aromatic (**3**), (b) one is aromatic and the other is quinoid (**1**), and (c) both rings are quinoid (**6**). The easier deformation from planarity of the quinoid rings leads, in comparison to **1**, to a much more pronounced boat-type deformation of the *para*-bridged ring the angles between the planes C(16) – C(11) – C(12) and C(13) – C(14) – C(15) with the basis plane C(12) – C(13) – C(15) – C(16) being 17.0 and 18.4°, respectively. Since the deformation of the *meta*-bridged ring in **6** is very similar to that of **1**, the transanular distances in **6** are, with the exception of the distances between the bridge-heads [C(3) ··· C(14): 275.7(2), C(7) ··· C(11): 277.4(2) pm], generally longer than in **1** and **3**. The inclination of 20° between the basis planes of the *meta*- and *para*-bridged rings in **6** is similar to that in **1**. The fact that of the three [2.2]metaparacyclophanes compared here the tendency to approach parallelity between the two rings is highest for **3** (inclination 13°) must be considered as the result of the specific steric interaction of the methoxy group on C(8) which has been discussed before.

Figure 3 A shows a top-view of **6** together with the bond lengths; Figure 3 B presents a side-view. Bond angles and some selected torsional angles are listed in Table 7.

Table 7. Bond Angles of **6** (Estimated Standard Deviations are Given in Parentheses in Units of the Last Quoted Digits)

C(2) – C(1) – C(14)	107.9(1)	C(6) – C(7) – C(9)	124.3(1)	C(11) – C(12) – O(12')	121.6(1)
C(1) – C(2) – C(3)	111.9(1)	C(8) – C(7) – C(9)	118.3(1)	C(13) – C(12) – O(12')	121.1(1)
C(2) – C(3) – C(4)	124.4(1)	C(3) – C(8) – C(7)	118.8(1)	C(12) – C(13) – C(14)	121.6(1)
C(2) – C(3) – C(8)	118.1(1)	C(3) – C(8) – O(8')	119.8(1)	C(1) – C(14) – C(13)	122.0(1)
C(4) – C(3) – C(8)	117.5(1)	C(7) – C(8) – O(8')	121.4(1)	C(1) – C(14) – C(15)	118.7(1)
C(3) – C(4) – C(5)	122.2(1)	C(7) – C(9) – C(10)	113.1(1)	C(13) – C(14) – C(15)	118.4(1)
C(4) – C(5) – C(6)	117.3(1)	C(9) – C(10) – C(11)	108.3(1)	C(14) – C(15) – C(16)	117.1(1)
C(4) – C(5) – O(5')	121.2(1)	C(10) – C(11) – C(12)	117.5(1)	C(14) – C(15) – O(15')	120.8(1)
C(6) – C(5) – O(5')	121.3(1)	C(10) – C(11) – C(16)	123.4(1)	C(16) – C(15) – O(15')	121.7(1)
C(5) – C(6) – C(7)	122.4(1)	C(12) – C(11) – C(16)	118.1(1)	C(11) – C(16) – C(15)	121.3(1)
C(6) – C(7) – C(8)	117.4(1)	C(11) – C(12) – C(13)	116.9(1)		

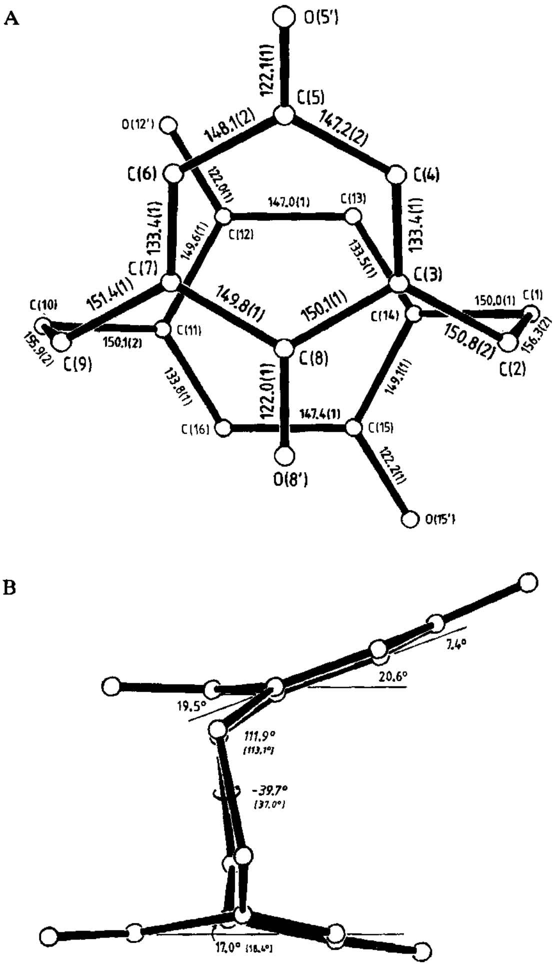


Figure 3. Molecular Structure of **6** in a Top-View Perpendicular to the *para*-Bridged Ring (A) and in a Side-View (B)

Charge-Transfer Absorptions of 1 and 2; Enantiomer Separation and Circular Dichroism of 1

In the electron spectrum, the tetramethoxy[2.2]metaparacyclophane has its long-wavelength absorptions at λ_{max} = 316 nm (ε = 2100) and 293 nm (ε = 2760), in chloroform. These absorptions are very well consistent with the absorptions of the two 2,5-dimethoxyxylenes and with the tetramethoxy[2.2]paracyclophanes[4]. Both **1** and **2** show strong broad structureless charge-transfer (CT) absorptions of which the CT band of **1** is observed at longer wavelength [λ_{max} = 490 nm (ε = 590)] than that of **2** [λ_{max} = 420 nm (ε = 825), in chloroform]. In comparison to the isomeric pseudogeminal- and pseudoortho-quinhydrones of the [2.2]paracyclophane series[4] the data of **1** are similar to the pseudogeminal [2.2]paracyclophane quinhydrone whereas the absorption of **2** occurs at shorter wavelength and shows considerably higher intensity than is observed for the pseudoortho-isomer. Any theoretical treatment of the CT absorptions of **1** and **2** in analogy to our HMO calculations on paracyclophane quinhydrones[8] is complicated by the facts that the hydroquinone and quinone rings of **1** and **2** are neither planar nor parallel to each other and that corresponding atoms of the donor and acceptor units are far from being arranged in ecliptic positions and in a symmetrical version common to both subunits.

As mentioned before, [2.2]metaparacyclophane quinhydrone **1** crystallizes – besides in at least two modifications of the racemate – with separated enantiomers in the chiral space group $P2_12_12_1$. On the basis of this observation a separation in dextro- and levorotatory enantiomers has been achieved by picking out single crystals. For two typical crystals of opposite chirality the optical rotations listed in Table 8 have been determined.

Table 8. Molar Rotation of Two Enantiomeric Single Crystals of **1** in Chloroform

	Crystal A[a]	Crystal B[b]
$[\Phi]_{460}^{20}$	-5215	$+5811$
$[\Phi]_{334}^{20}$	-35164	$+41720$

[a] $c = 2.8 \cdot 10^{-6}$ g/ml; [b] $c = 2.1 \cdot 10^{-6}$ g/ml.

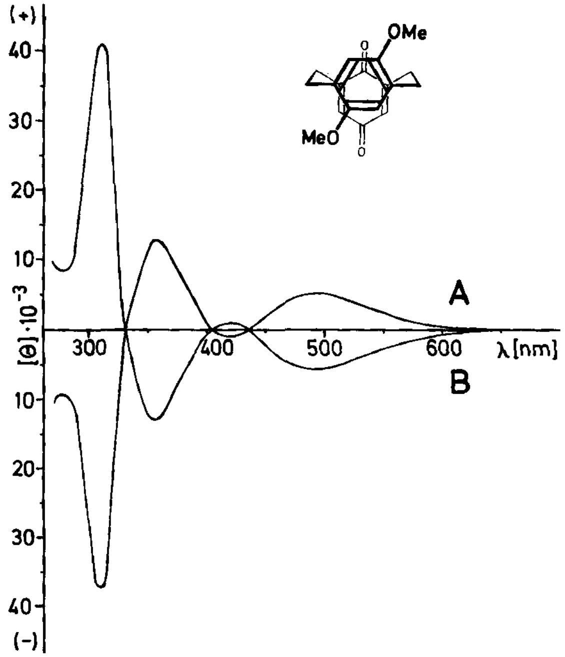


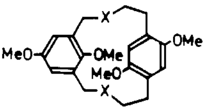
Figure 4. Circular Dichroism of Two Enantiomeric Single Crystals A and B of **1** in Chloroform (A: $c = 2.8 \cdot 10^{-6}$ g/ml; B: $c = 2.1 \cdot 10^{-6}$ g/ml; JASCO J 500)

From solutions of two enantiomeric crystals of **1** in chloroform the circular dichroism was measured which to our knowledge is the first determination of CD related to charge-transfer chromophors with well-defined donor-acceptor orientation (Figure 4). A better understanding of charge-transfer-related CD may supply valuable information for assigning charge-transfer absorptions, especially in those cases where more than one CT-transitions are expected to contribute to the generally very broad CT absorption bands[8,9].

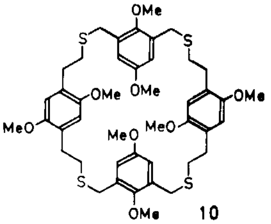
Synthesis, Molecular Structure and Charge-Transfer Absorptions of Quinhydrones of the [3.3]Metaparacyclophane Series

In comparison to [2.2]metaparacyclophanes the steric strain in [3.3]metaparacyclophanes is considerably reduced. As a result the molecular structures including the donor-acceptor overlap in quinhydrones of the [3.3]metaparacyclophane series should be quite different from those in the lower homologous series. A comparison of corresponding derivatives of these two series therefore seemed worthwhile.

Synthesis: The synthesis of [3.3]metaparacyclophane quinhydrones was achieved in close analogy to that of the [2.2]series. Cyclisation of 1,4-bis(2-mercaptoethyl)-2,5-dimethoxybenzene with 1,3-bis(bromomethyl)-2,5-dimethoxybenzene (potassium carbonate, boiling methanol/tetrahydrofuran, high dilution) led in 50% yield to the dithia[4.4]metaparacyclophane **9**; in addition, compound **10** was formed in variable yield. Analytical and spectroscopic data are given in the Experimental Part.

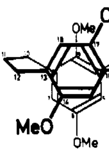


9 : X = S
11 : X = SO_2

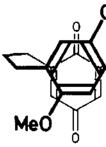


10

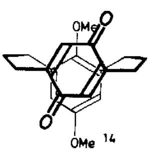
Oxidation of **9** (*m*-chloroperbenzoic acid, dichloromethane, 4 h, 20°C; 59%) yielded the disulfone **11** from which by vapour-phase pyrolysis 6,9,14,17-tetramethoxy[3.3]-metaparacyclophane (**12**) was obtained (55% yield; m.p. 122°C). Analytical and spectroscopic data given in the Experimental Part support structure **12**. In addition to **12** the two quinhydrones **13** (20% yield) and **14** (4% yield) were isolated as by-products; alternative attempts to prepare these compounds by partial demethylation of **12** and subsequent oxidation are reported below.



12



13



14

Neither the mass spectra nor the ^1H NMR spectra allow a clear assignment to the structures **13** and **14** [MS: **13**: m/z = 326 (100%, M^+), 177 (56), 164 (19), 162 (33), 147 (20), 136 (10); **14**: m/z = 326 (100%, M^+), 149 (16). – ^1H NMR (80 MHz, $CDCl_3$): **13**: δ = 1.8 – 3.4 (m, 12H), 3.52 (s, 3H), 3.88 (s, 3H), 6.19 (m, 1H), 6.28 (s, 1H), 6.29 (m, 1H), 6.52 (s, 1H); **14**: δ = 1.8 – 4.0 (m, 12H), 3.51 (s, 3H), 3.73 (s, 3H), 5.59 (s, 1H), 6.40 and 6.52 (AB, J_{AB} = 3.2 Hz, 2H), 6.57 (s, 1H)]. An unequivocal structure determination has been reached, however, by an X-ray structure analysis of **13** (see below).

Partial demethylation of **12** with boron tribromide and subsequent oxidation with silver oxide resulted in the formation of **14** in small amounts (2.4% yield) besides traces

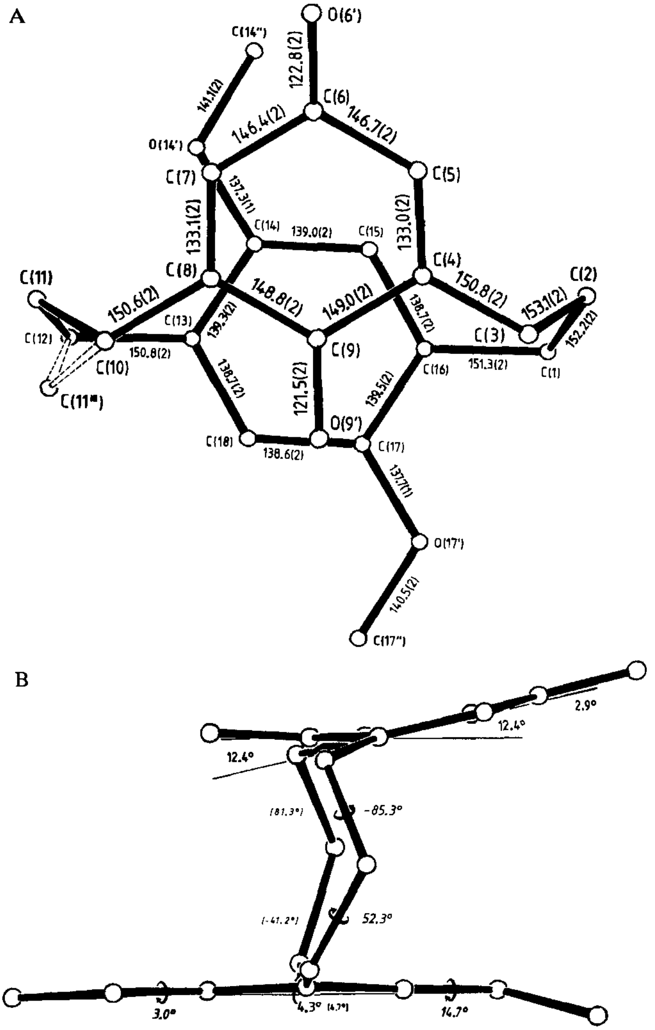
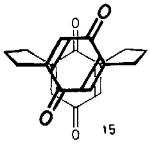


Figure 5. Molecular Structure of **13** in a Top-View Perpendicular to the *para*-Bridged Ring (A) and in a Side-View (B)

of **13**. Partial oxidative ether cleavage of **12** with diammonium-hexanitratocerate (acetonitrile, 6 h, 20°C) led to **14** in 15% yield; in this case **13** was not isolated at all. In contrast to these reactions the complete demethylation of **12** with boron tribromide (dichloromethane, 30 min, 20°C) yielded after oxidation with silver oxide (acetone, 4 d, 20°C) [3.3](2,5)-(2,6)-*p*-benzoquinonophane (**15**) in excellent yield (80%). Elemental analyses and spectroscopic data listed in the Experimental Part prove the structure suggested. As with the bis(quinone) **6** in the [2.2]metaparacyclophane series, attempts to partially hydrogenate **15** to one of the quinhydrones corresponding to either **13** or **14** led to a mixture of both which was not separated.



15

X-Ray Structure Analysis of **13**: For the structure analysis monoclinic crystals of space group $P2_1/c$ were used: a = 855.5(1), b = 2569.7(3), c = 837.0(1) pm, β = 114.87(2)°; Z = 4, D_x = 1.30 gcm^{-3}. Data collection as above; 4473 measured reflections, 3050 reflections with $I \geqslant 1.96\sigma(I)$. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares technique using anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms. On the basis of a difference Fourier synthesis, for the central atom C(11) of the one methylene bridge a second atomic position (disorder 15%) was established. R = 0.053.

Figure 5A shows the molecular structure of **13** in a top-view perpendicular to the *para*-bridged ring; in Figure 5B a side-view is shown. The longer bridges as compared to **1** have some major effects: The first is that the overlap between the quinone and the aromatic donor is considerably less than in **1**. Further differences are due to the strong reduction in steric strain as a consequence of which the *para*-bridged aromatic ring

Table 9. Atomic Coordinates and Thermal Parameters $U_{equ.}$ (in pm^2) of Non-Hydrogen Atoms of **13** (Numbers in Parentheses are Estimated Standard Deviations in the Last Quoted Digits)

Atom	x	y	z	Uequ.	Atom	x	y	z	Uequ.
C(1)	0.0047(2)	0.36897(6)	0.4015(2)	482(5)	C(12)	0.4452(2)	0.29405(6)	0.0793(2)	556(5)
C(2)	0.0001(2)	0.42800(6)	0.3050(2)	600(6)	C(13)	0.3420(2)	0.30660(6)	0.1027(2)	443(5)
C(3)	-0.0346(2)	0.44839(7)	0.2012(2)	708(7)	C(14)	0.4074(2)	0.33744(5)	0.3335(2)	412(4)
C(4)	0.1240(2)	0.45277(6)	0.1676(2)	543(5)	C(15)	0.2905(2)	0.35541(5)	0.4064(2)	416(4)
C(5)	0.2511(2)	0.48620(6)	0.2535(2)	608(6)	C(16)	0.1249(2)	0.34265(5)	0.3361(2)	410(4)
C(6)	0.4111(2)	0.48863(6)	0.2294(2)	603(6)	C(17)	0.0630(2)	0.30781(6)	0.1953(2)	466(5)
C(7)	0.4320(2)	0.45036(7)	0.1103(2)	604(6)	C(18)	0.1716(2)	0.29080(6)	0.1203(2)	490(5)
C(8)	0.3093(2)	0.41652(6)	0.0180(2)	552(5)	C(14*)	0.6563(2)	0.37204(8)	0.5662(2)	744(7)
C(9)	0.1398(2)	0.42014(6)	0.0275(2)	564(6)	C(17*)	-0.1719(2)	0.25064(8)	-0.0000(3)	912(8)
C(10)	0.3321(3)	0.37743(7)	-0.1046(2)	747(7)	O(6')	0.5239(2)	0.52068(5)	0.3080(2)	865(5)
C(11) a)	0.4786(2)	0.34074(8)	-0.0166(2)	640(7)	O(9')	0.0135(2)	0.39859(5)	-0.0014(2)	840(6)
C(11*) b)	0.358(1)	0.3217(4)	-0.102(1)	550(40)	O(14')	0.5787(1)	0.35025(4)	0.3971(1)	555(4)
a) g = 0.85(2) ; b) g = 0.15(2)					O(17')	-0.1070(1)	0.29365(4)	0.1333(1)	676(4)

deviates only very slightly from planarity [C(13) and C(16): 4.5°], and the inclination between the bases of the two rings amounts to only 12.4°. All transanular distances between ring atoms including the pairs of bridge-head atoms are longer than 310 pm.

Table 10. Bond Angles of **13** (Estimated Standard Deviations are Given in Parentheses in Units of the Last Quoted Digits)

C(2) - C(1) - C(16)	114.1(1)	C(7) - C(8) - C(10)	122.3(2)	C(13) - C(14) - O(14')	116.3(1)
C(1) - C(2) - C(3)	114.8(1)	C(9) - C(8) - C(10)	119.1(1)	C(15) - C(14) - O(14')	123.6(1)
C(2) - C(3) - C(4)	113.9(1)	C(4) - C(9) - C(8)	119.0(1)	C(14) - C(15) - C(16)	122.0(1)
C(3) - C(4) - C(5)	122.7(2)	C(4) - C(9) - O(9')	120.2(1)	C(1) - C(16) - C(15)	120.7(1)
C(3) - C(4) - C(9)	119.3(1)	C(8) - C(9) - O(9')	120.7(1)	C(1) - C(16) - C(17)	121.5(1)
C(5) - C(4) - C(9)	118.0(1)	C(8) - C(10) - C(11)	114.1(2)	C(15) - C(16) - C(17)	117.7(1)
C(4) - C(5) - C(6)	123.1(2)	C(10) - C(11) - C(12)	116.7(2)	C(16) - C(17) - C(18)	120.1(1)
C(5) - C(6) - C(7)	116.9(1)	C(11) - C(12) - C(13)	114.5(1)	C(16) - C(17) - O(17')	116.5(1)
C(5) - C(6) - O(6')	121.6(2)	C(12) - C(13) - C(14)	122.2(1)	C(18) - C(17) - O(17')	123.3(1)
C(7) - C(6) - O(6')	121.5(1)	C(12) - C(13) - C(18)	119.9(1)	C(13) - C(18) - C(17)	122.1(1)
C(6) - C(7) - C(8)	122.8(2)	C(14) - C(13) - C(18)	117.7(1)	C(14) - O(14')- C(14'')	117.6(1)
C(7) - C(8) - C(9)	118.5(1)	C(13) - C(14) - C(15)	120.0(1)	C(17) - O(17')- C(17'')	117.8(1)

Bond lengths of **13** are given in Figure 5 A. Bond angles and some specific torsional angles are listed in Table 10.

Charge-Transfer Absorptions of **13** *and* **14**: For **13** the first CT-band is similar to that of **1**: λ_{max} = 485 nm (ε = 560); at shorter wavelength, however, a second maximum is observed at 375 nm (ε = 620) which obviously has to be assigned to a second CT transition which is also found in the electronic spectra of pseudoortho[3.3]paracyclophane quinhydrones. As for the pair of structural isomers **1**/**2**, for the corresponding pair in the [3.3]series **14**, homologous to **2**, shows a CT absorption at considerably shorter wavelength [λ_{max} = 365 nm (ε = 800), all data in chloroform] explaining the orange colour of the **14**-crystals as compared to the dark-red of **13**. As mentioned for the CT absorptions of **1**/**2**, the rather complex, unsymmetrical structure of the meta-paracyclophane system excluded an explanation of these results on the basis of a simple HMO model which worked fairly well for the [2.2]- and [3.3]paracyclophane quinhydrones.

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Experimental Part

6,9,14,17-Tetramethoxy-2,11-dithia[3.3]metaparacyclophane (**4**): Solutions of 16.2 g (50 mmol) of 1,3-bis(bromomethyl)-2,5-dimethoxybenzene[10] in 1000 ml of tetrahydrofuran and of 11.5 g (50 mmol) of 1,4-bis(mercaptomethyl)-2,5-dimethoxybenzene[11] in 1000 ml of dimethylformamide were added synchronously over 16 h to a boiling mixture of 500 ml of tetrahydrofuran and 500 ml of dimethylformamide to which 50 g of potassium carbonate had been added. After cooling the reaction mixture was filtered, evaporated in vacuo to about half its volume and given into a mixture of 2 l of water and 100 ml of diluted hydrochloric acid. The precipitate was dried and chromatographed from chloroform on silica: 3.5 g (43%) of **4**, m. p. 163.5°C. – ^{1}H NMR

(80 MHz, $CDCl_3$): δ = 3.1 – 4.7 (m, 8H), 3.32 (s, 3H), 3.44 (s, 3H), 3.75 (s, 3H), 3.85 (s, 3H), 6.06 (s, 1H), 6.60 (s, 1H), 6.75 („s", 2H).

$C_{20}H_{24}O_4S_2$ (392.4) Calcd. C 61.21 H 6.17 S 16.34
Found C 61.35 H 6.40 S 16.18 Molecular mass 392 (M^+, MS)

6,9,14,17-Tetramethoxy-2,11-dithia[3.3]metaparacyclophane-2,2,11,11-tetraoxide (**5**): 1.00 g (2.55 mmol) of **4** in 10 ml of dichloromethane was added to 20 ml of a solution of hydrogen peroxide (60%) in water and 1 ml of acetic acid. This two-phase system was vigorously stirred at 20°C until under evaporation of the dichloromethane **5** precipitated: 1.03 g (89%); pure crystals of **5** were obtained from chloroform; dec. > 280°C.

$C_{20}H_{24}O_8S_2$ (456.4) Calcd. C 52.63 H 5.30 S 14.05
Found C 52.43 H 5.55 S 13.90 Molecular mass 456 (M^+, MS)

5,8,12,15-Tetramethoxy[2.2]metaparacyclophane (**3**): 1.00 g (2.19 mmol) of **5** were pyrolyzed at 520°C/0.004 Torr in a pyrolysis apparatus[6)] (evaporation zone: 280°C, 40 min). The pyrolysis product precipitated at the cooling finger was dissolved in dichloromethane and chromatographed on silica: 575 mg (80%) of **3**, recrystallized from ligroin (60 – 95°C): m.p. 112 – 113°C. – ^1H NMR: see above.

$C_{20}H_{24}O_4$ (328.4) Calcd. C 73.14 H 7.37
Found C 73.26 H 7.50 Molecular mass 328 (M^+, MS)

12,15-Dimethoxy[2](2,6)-p-benzoquinono[2]paracyclophane (**1**): a) To a methylmagnesium iodide solution, prepared from 750 mg (30 mmol) of magnesium and 4.4 g (30 mmol) of iodomethane in 50 ml of ether, 820 mg (2.5 mmol) of **3** in 15 ml of toluene was added. After evaporation of the solvents the reaction mixture was heated for 1 h to 150 – 160°C. Careful hydrolysis by water and diluted sulfuric acid and extraction with ether led to an extract which was dried and evaporated. The residue was dissolved in 20 ml of acetone and stirred at 20°C for 12 h with 4.8 g (20 mmol) of silver oxide. Chromatography from chloroform on silica yielded 230 mg (30%) of **1** in dark rubin-red crystals of m.p. 142°C (from ethanol). – ^1H NMR and MS: see Theoretical Part.

$C_{18}H_{18}O_4$ (298.3) Calcd. C 72.46 H 6.08 Found C 72.45 H 6.24

b) In the pyrolysis of **5** mentioned above by the chromatography yielding mainly **3** 10 mg (1.5%) of **1** in dark-red crystals of m.p. 142°C was obtained which was identified with the product obtained in the aforementioned procedure a).

13,16-Dimethoxy[2](2,5)-p-benzoquinono[2]metacyclophane (**2**): From the pyrolysis leading to **3** (see above) as a side-product by chromatography from dichloromethane on silica 13 mg (1.9%) of **2** in orange crystals of m.p. 171°C was obtained. – ^1H NMR and MS: see Theoretical Part.

$C_{18}H_{18}O_4$ (298.3) Calcd. C 72.46 H 6.08 Found C 72.45 H 6.24

[2.2](2,5)-(2,6)-p-Benzoquinonophane (**6**): To 328 mg (1 mmol) of **3** in 10 ml of dichloromethane under nitrogen 2 g (8 mmol) of boron tribromide was added. After 45 min stirring at 20°C and careful hydrolysis dichloromethane was added, the organic phase was separated and the aqueous solution was extracted with dichloromethane. The combined dichloromethane fractions were dried on sodium sulfate, the solvent was evaporated in vacuo, the residue was dissolved in 20 ml of acetone and stirred for 12 h with 475 mg (2 mmol) of silver oxide. Filtration, evaporation of the solvent and recrystallisation of the residue from ligroin (60 – 95°C) yielded 185 mg (70%) of **6** in yellow crystals, m.p. 197°C. – ^1H NMR (80 MHz, $CDCl_3$): δ = 2.1 – 3.5 (m, 8H), 6.23 (s, 1H), 6.37 (d, 1H), 6.48 (s, 1H), 6.51 (s, 1H).

$C_{16}H_{12}O_4$ (268.3) Calcd. C 71.63 H 4.51
Found C 71.43 H 4.23 Molecular mass 268 (M^+, MS)

6,9,17,20-Tetramethoxy-2,13-dithia[4.4]metaparacyclophane (**9**): Solutions of 2.60 g (10 mmol) of 1,3-bis(bromomethyl)-2,5-dimethoxybenzene and of 3.64 g (10 mmol) of 1,4-bis(2-mercaptoethyl)-2,5-dimethoxybenzene in 1000 ml of methanol/tetrahydrofuran (9:1) each, were simultaneously added within 16 h to 1 l of boiling methanol containing 5 g of potassium carbonate. After cooling, filtration and evaporation of the solvents the residue was extracted with dichloromethane and chromatographed on silica. The first fraction obtained was 2.1 g (50%) of **9**, m. p. 142°C (from ligroin, 60–95°C). – ^1H NMR (80 MHz, $CDCl_3$): δ = 1.8–4.7 (m, 12H), 3.55 (s, 3H), 3.62 (s, 3H), 3.70 (s, 3H), 3.76 (s, 3H), 6.20 (s, 1H), 6.40 and 6.61 (AB, J = 3.20 Hz, 2H), 6.47 (s, 1H). – MS: m/z = 420 (100%, M^+), 209 (20), 195 (18), 165 (52), 149 (42).

$C_{22}H_{28}O_4S_2$ (420.4) Calcd. C 62.84 H 6.71 S 15.25 Found C 62.79 H 6.67 S 14.96

By the chromatographic separation mentioned before, as a by-product **10** (R_F about 0.5 of that of **9**) was obtained in variable yield; m. p. 177°C (from cyclohexane).

$C_{44}H_{56}O_8S_4$ (840.8) Calcd. C 62.84 H 6.71 S 15.25
Found C 62.79 H 6.76 S 15.34 Molecular mass 840 (M^+, MS)

6,9,17,20-Tetramethoxy-2,13-dithia[4.4]metaparacyclophane-2,2,13,13-tetraoxide (**11**): To 3.1 g (7.3 mmol) of **9** in 450 ml of dichloromethane 7 g (40 mmol) of *m*-chloroperbenzoic acid was added at 20°C. After 4 h stirring the solvent was removed by evaporation, the residue was washed with aqueous sodium hydroxide solution and water: 2.1 g (59%) of **11**, dec. > 280°C. – ^1H NMR (80 MHz, $CDCl_3$): δ = 2.3–4.8 (m, 12H), 3.43 (s, 3H), 3.44 (s, 3H), 3.78 (s, 3H), 3.81 (s, 3H), 6.20 (s, 1H), 6.62 (s, 1H), 6.84 and 7.14 (AB, J = 2.97 Hz, 2H). – MS: m/z = 484 (100%, M^+), 356 (29), 191 (57), 177 (22), 165 (25), 149 (34).

$C_{22}H_{28}O_8S_2$ (484.4) Calcd. C 54.54 H 5.83 S 13.23 Found C 54.25 H 5.90 S 13.43

6,9,14,17-Tetramethoxy[3.3]metaparacyclophane (**12**): 0.5 g (1 mmol) of **11** was pyrolyzed at 560°C/0.004 Torr in a pyrolysis apparatus⁶⁾ (evaporation zone: 290°C, 30 min). The products precipitated at the cooling finger were dissolved in dichloromethane and separated by chromatography on silica. The product migrating fastest was crystallized from ethanol: 203.5 mg (55%) of **12**, colourless crystals, m. p. 122°C. – ^1H NMR (80 MHz, $CDCl_3$): δ = 1.8–3.3 (m, 12H), 3.26 (s, 3H), 3.33 (s, 3H), 3.71 (s, 3H), 3.83 (s, 3H), 5.63 (s, 1H), 6.28 and 6.34 (AB, J = 3.3 Hz, 2H), 6.53 (s, 1H). – MS: m/z = 356 (100%, M^+), 178 (21, M^{2+}), 166 (12), 151 (10).

$C_{22}H_{28}O_4$ (356.4) Calcd. C 74.13 H 7.92 Found C 74.40 H 8.15

14,17-Dimethoxy[3](2,6)-p-benzoquinono[3]paracyclophane (**13**): a) In the aforementioned chromatography (silica, dichloromethane) of the pyrolysis products from **11** 66 mg (20%) of **13** was obtained; red crystals, m. p. 172.5°C (from methanol).

b) To a solution of 89 mg (0.25 mmol) of **12** in 20 ml dichloromethane under nitrogen 0.05 ml (0.5 mmol) of boron tribromide was added. After stirring at 20°C for 30 min the reaction mixture was hydrolysed, extracted with dichloromethane, the combined dichloromethane solutions dried and evaporated. The residue was dissolved in 20 ml of acetone, 0.5 g (2 mmol) of silver oxide was added, and the suspension was stirred for 12 h. After filtration and evaporation, from the mixture of products by preparative DC besides 2 mg (2.4%) of **14** about 1 mg of **13** was isolated and identified with the product obtained according to a). – ^1H NMR and MS: see Theoretical Part.

$C_{20}H_{22}O_4$ (326.4) Calcd. C 73.60 H 6.79 Found C 73.72 H 6.63

15,18-Dimethoxy[3](2,5)-p-benzoquinono[3]metacyclophane (**14**): a) From the chromatography of the pyrolysis products of **11** (see above) a third fraction was obtained which after crystallisation from ligroin (60–95°C) yielded 10 mg (4%) of **14** as orange crystals, identical with the product obtained according to the following procedure.

b) To 71 mg (0.2 mmol) of **12** in 20 ml acetonitrile a solution of 300 mg (0.54 mmol) of diammonium-hexanitratocerate in a small amount of water was added. After 6 h stirring at 20°C the reaction mixture was extracted with dichloromethane, and the extract was chromatographed from dichloromethane in preparative DC on silica plates. Besides 7 mg (10%) of **12**, 10 mg (15%) of **14**, yellow crystals, m. p. 122°C, was obtained. – ^{1}H NMR and MS: see Theoretical Part.

$C_{20}H_{22}O_4$ (326.4) Calcd. C 73.60 H 6.79 Found C 73.52 H 6.63

[3.3](2,5)-(2,6)-p-Benzoquinonophane (**15**): To a solution of 178 mg (0.5 mmol) of **12** in 20 ml dichloromethane under nitrogen 0.4 ml (4 mmol) of boron tribromide was added. After 30 min stirring at 20°C the reaction was hydrolysed, dichloromethane was added and the phases separated. The aqueous phase was extracted with ether, combined with the dichloromethane solution, dried and evaporated. The residue was dissolved in 30 ml of acetone and stirred for 4 d at 20°C as a suspension with 240 mg (1 mmol) of silver oxide. After filtration and evaporation the product obtained was chromatographed from dichloromethane on silica: 125 mg (80%) of **15**, yellow crystals, dec. > 180°C. – ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 1.7-3.1$ (m, 12H), 6.22 (m, 1H), 6.48 (s, 2H), 6.54 (d, $J = 1.37$ Hz, 1H). – MS: $m/z = 296$ (100%, M^+), 279 (12), 173 (12), 160 (40), 149 (63), 147 (38), 136 (53).

$C_{18}H_{16}O_4$ (296.3) Calcd. C 72.96 H 5.44 Found C 72.97 H 5.57

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1) Part XXXV: *H. Bauer, J. Briaire,* and *H. A. Staab,* Angew. Chem. **95**, 330 (1983); Angew. Chem., Int. Ed. Engl. **22**, 334 (1983) [this paper, erroneously, has been referred to as Part XXXIV whereas, in fact, Part XXXIV had already been assigned to the publication *H. A. Staab, B. Starker,* and *C. Krieger,* Chem. Ber. **116**, 3831 (1983)].

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7) Further information concerning the X-ray structure analyses of **1**, **3**, **6**, and **13** may be requested from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, with indication of the registry number CSD 50761, the author's name, and the reference to this publication.

8) *H. Vogler, G. Ege,* and *H. A. Staab,* Tetrahedron **31**, 2441 (1975).

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