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New Tetraoxacyclophanes with α,α′-Di(para-hydroxyphenyl)-1,4-diisopropylbenzene Structural Unit

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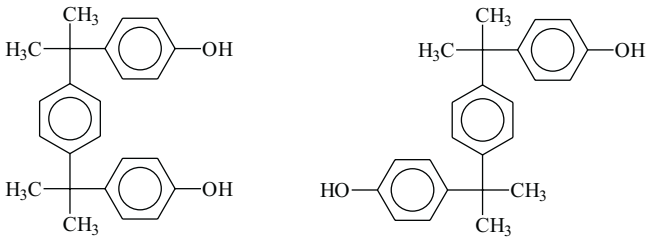
α,α′-Di(para-hydroxyphenyl)-1,4-diisopropylbenzene (**1**) was used as a precursor for synthesis of six macrocyclic compounds (**5**–**10**). Low-temperature crystal structures were determined for α,α′-di(4-ethoxyphenyl)-1,4-diisopropylbenzene (**3**), $C_{30}H_{38}O_2$, monoclinic $P2_1/c$, a = 12.831(4), b = 8.708(2), c = 11.221(3) Å, Z = 2, and 32,32,39,39-tetramethyl-13-oxo-1,6,20,25-tetraoxa[6.1.6.1.1]paracyclophane (**7**), $C_{49}H_{53}O_5$, triclinic $P\bar{1}$, a = 10.506(2), b = 14.770(2), c = 14.917(2) Å, α = 111.91(2), β = 108.75(2), γ =95.30(2)°, Z = 2. Compound **7** forms 2:1 clathrate-type compound with *para*-xylene. IR, Raman and UV spectra were recorded for all compounds.

Key words: tetraoxacyclophanes, preparation, crystal structure, IR and Raman spectra

Molecular recognition is a rapidly developing branch of supramolecular chemistry. Newly synthesized compounds are becoming increasingly suited to the formation of complexes, and more and more these reflect processes taking place in living organisms. Their syntheses are also becoming increasingly complex. In search of simple "building blocks" for obtaining "host"-type compounds we first used a commercially-available 4,4′-dihydroxybenzophenone which, however, proved to be a rather unsatisfactory substrate for obtaining such compounds. The unfavorable mutual positioning of phenyl rings and unsuitable molecular packing in the crystal do not permit the uptake of neutral "guest" organic entities, either between the rings of the molecule or in the space between particular molecular layers in the crystal [1]. For these interactions to occur, suitable canals would be required in the crystallographic network in order to permit inclusion of small molecules. Alternatively, "host" binding sites would have to be reorganized during crystal formation. The situation is different for compounds containing "triphenyl" fragments of type **1** (for nomenclature reasons the whole fragment derived from compound **1** will be referred to as "triphenyl"). Host molecules formed from two such fragments can form clathrate-type compounds with neutral organic molecules. Small molecules such as CH_2Cl_2 can position themselves inside the host ring, whereas larger ones, such as *p*-xylene, are located in channels between cyclophane layers of the crystallographic network [2].

RESULTS AND DISCUSSION

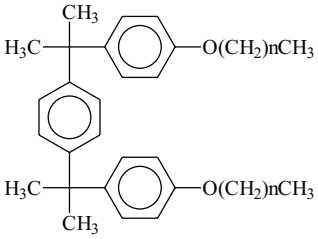
To synthesize tetraoxacyclophanes we used a triphenyl molecule **1** obtained according to [3]. Three model compounds, **2–4**, with differing alkyl substituents, were obtained. NMR spectra are not helpful in determining the conformation of the model compounds. The synthetic route chosen and model studies of compound **1** both suggest that the latter may occur in two different conformations referred to herein as *syn* and *anti*, as shown in Fig. 1.



1 – *syn* **1** – *anti*

Figure 1.

Compound **1** is obtained as amorphous solid, and we did not succeed in growing crystals suitable for crystallographic studies. Quantum chemical calculations and model studies (CPK) suggest that the barrier of **1**-*syn* to **1**-*anti*- transfer is appreciable (*ca.* 15 kcal/mol, as assessed by AM1 and PM3 methods, available in HyperChem standard version) and that both conformers of compound **1** should be obtained in the reaction mixture.

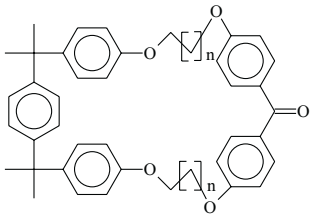


2–4 n = 1 – 3

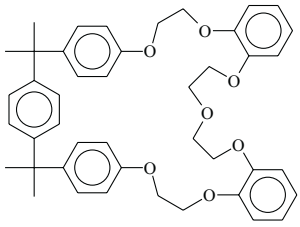
Figure 2.

The proof of the presence of the *anti* form in the reaction mixture came from studies of model (alkyl) derivatives **2–4** of the starting compound **1 (**Fig. 2). Attempts to obtain single crystals from these two compounds led us to compound **3**, in which all molecules were in the *anti* conformation. So far, we have not succeeded in obtaining *syn*-type crystals of model compounds that would be suitable for crystallographic studies. (Crystal data and molecular dimensions of **3-***anti* are given in Tables 5 and 6 in the crystallographic section). This open-ring model compound is not a representative example of structural elements present in the cyclic compound because only the

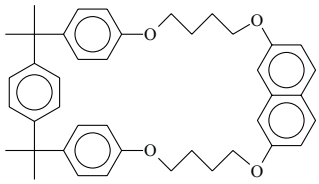
syn-form, with both outer phenyl rings adopting the "face-to-face" conformation, can yield a cyclic compound. The macrocyclic compounds obtained are shown in Fig. 3.



5 n = 1
6 n = 2
7 n = 3
8 n = 4



9



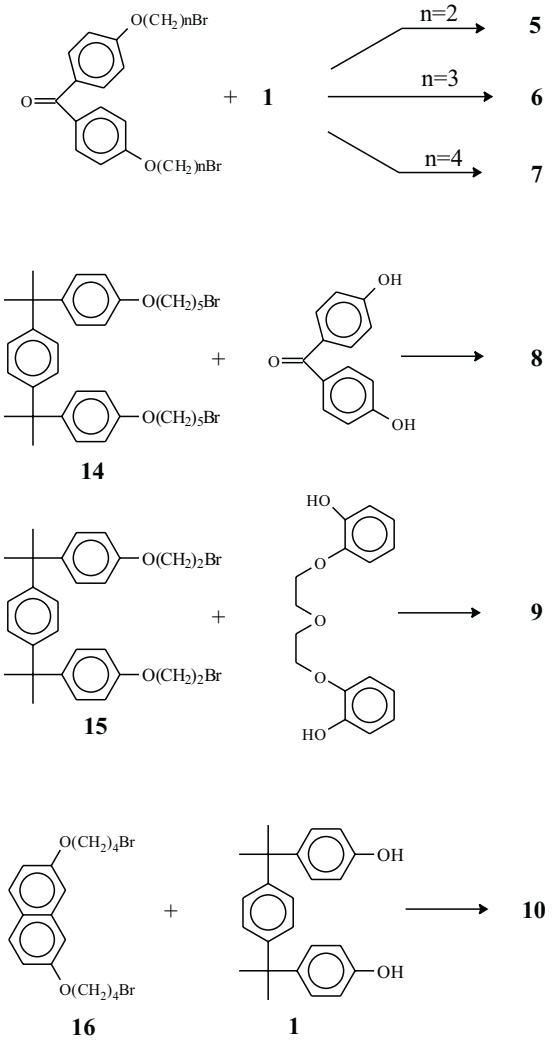
10

Figure 3.

The synthesis of macrocycles: All of the compounds investigated were synthesized according to Scheme 1. Since they contain two different aromatic fragments they can be formed from various starting compounds (in case of our syntheses their choice was random). The dibromo derivatives were cyclized with dihydroxyaromatic compounds in DMF at 50–60°C for several (generally 3–4) days in the presence of Cs_2CO_3. The compounds were obtained in 20–40% yield after chromatographic separation on silica gel. The cyclization reactions lead to considerable amounts of polymeric by-products. Changing reaction conditions causes no increase of yield. This may result from the two alternative conformations of compound **1** (Fig. 1).

Synthesis of dibromo-derivatives: The synthesis of dibromo-derivatives according to procedure [2] described in the Experimental section, even in the presence of a large excess of α,ω-dibromoalkane, yields, besides the main reaction product, a dibromo derivative with bromoalkyl chains attached to two different aromatic molecules linked by an alkyl chain (*eg*. **17** or **18** – Scheme 2). These compounds are obtained in > 20% yield. They would be good precursors to macrocycles with three aromatic "centers" (Fig. 4). Attempts to obtain such compounds are underway. Besides these two compounds, a small amount of a third, monosubstituted derivative of

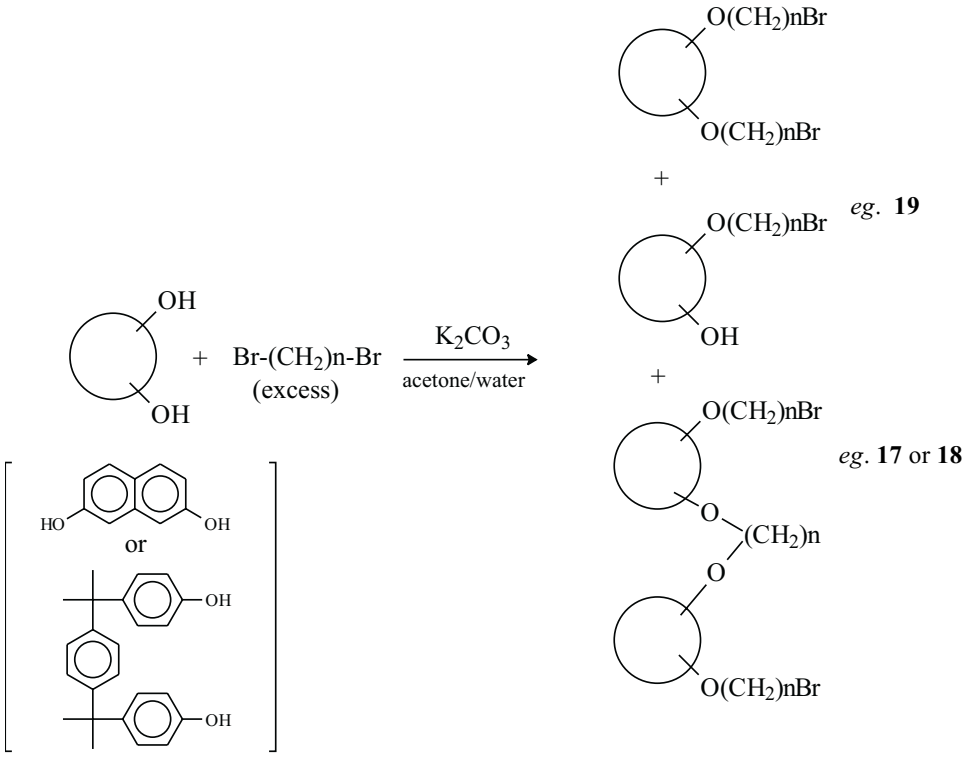
Scheme 1



the starting compound (for example **19**) could be isolated from the reaction mixture. The syntheses of dibromo-derivatives have not been optimized. Change of solvent to DMF did not increase the yield of di(bromoalkyl) derivatives. Besides the three isolated products, a certain amount of polymeric by-product is also formed, often separating out of solution during the reaction.

Synthesis of model compounds: The model compounds **2–4** were obtained by the reaction of **1** with a large excess of 1-bromoalkanes in acetone in the presence of K_2CO_3. Following column purification and crystallization from *para*-xylene or methanol, we obtained analytically pure compounds (in case of compound **3** crystals suitable for X-ray studies were obtained from *para*-xylene; see Fig. 5).

Scheme 2



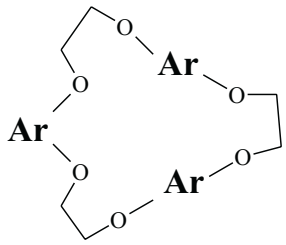
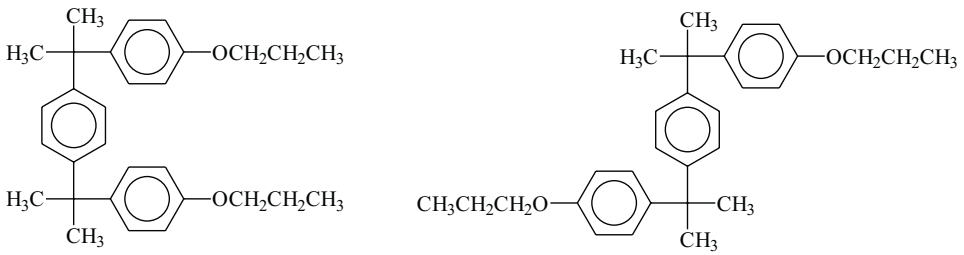


Figure 4.



3 - *syn* **3** - *anti*

Figure 5.

NMR spectra: Table 1 presents the NMR data. The ^{1}H NMR spectra are typified by the constant presence of triphenyl fragment peaks (singlet at $\delta \sim 7.1$ppm) with signals from the central phenyl ring protons and by a *doublet of doublets* at $\delta \sim 6.8$ and 7.1 ppm, derived from protons of the outer phenyl rings with a coupling constant J = 8.8 Hz. All remaining peaks are found at the expected positions. Attempts to determine mutual interactions of macrocyclic molecules with other neutral organic molecules failed. No change of signal location was detected either for the macrocycles or the neutral molecules introduced. Table 1 also gives the ^{13}C NMR signals as measured in $CDCl_3$.

Mass spectra: Mass spectra of macrocyclic compounds are not always easily obtainable. Because of their high boiling points they are not amenable to the EI method. Often, only fragmentary ions with low mass can be obtained. Much better are methods relying on other ionization sources (ions, molecules) that do not cause molecular fragmentation. Obtaining mass spectra with EI source was attempted for all the compounds synthesized (**2–10**). Only in case of compound **9** was a molecular ion recorded; its intensity, however, was very low (~ 4%). The most intensive ion was that with m/z = 136, derived from 1,2-dihydroxybenzene. Mass spectra of the remaining compounds were acquired using ESI or LSIMS techniques. These methods yields distinct $(M+H)^+$ ions. Far better results, though, are obtained by detecting $(M+Na)^+$ ions, when a sample of the compound is ionized in the presence of sodium ions. The results obtained for particular compounds are given in the Experimental section.

IR and Raman spectra: For all compounds **1–10** solid state IR and Raman spectra were obtained (Tables 2 and 3). A comparison of IR spectra of compounds **5–8**, which differ in the number of carbon atoms in the bridges, allows the following conclusions: in the stretching vibrations (region *ca*. 3050–2850 cm^{-1}) no clear shift changes of particular bands are seen (for both aromatic and aliphatic fragments). For compounds **5–8** characteristic vibrations are those of the carbonyl group occurring at ν_{CO} = 1657 cm^{-1} for **5**, 1649 cm^{-1} for **6**, 1637 cm^{-1} (shoulder at 1648 cm^{-1}) for **7** and 1640 cm^{-1} for **8**. Concomitant with the size increase of the central macrocycle ring, there occurs a

Table 1. ^{1}H NMR and ^{13}C NMR spectra of compounds **1–10**.

	H_{aromat}	$H_{bridges}$	H_{alifat}	C_{alifat}	C_{aromat}	C=O
1	6.70, 7.08 dd (8H, J = 8.7 Hz), 7.07 s (4H)		1.61 s (12H)			
2	6.79, 7.14 dd (8H, J = 8.8 Hz), 7.09 s (4H)		1.39 t (6H), 1.63 s (12H), 3.99 q (4H)	14.9, 30.8, 41.8, 63.2	113.7, 126.1, 127.7, 142.7, 147.8, 156.6	
3	6.79, 7.10 dd (8H, J = 8.8 Hz), 7.09 s (4H)		1.01 t (6H), 1.63 s (12H), 1.77 q (4H), 3.87 t (4H)	11.8, 23.8, 32.1, 42.9, 70.5	114.9, 127.3, 128.9, 143.9, 149.0, 158.0	
4	6.78, 7.13 dd (8H, J = 8.9 Hz), 7.09 s (4H)		0.96 t (6H), 1.55 sext (4H), 1.63 s (12H), 1.75 sext (4H), 3.92 t (4H)	13.8, 19.2, 31.0, 31.4, 41.8, 67.5	113.7, 126.2, 127.7, 142.7, 147.8, 156.9	
5	6.78, 7.67 dd (8H, J = 8.8 Hz), 6.99, 7.13 dd (8H, J = 8.8 Hz), 7.11 s (4H)	4.30 t (4H), 4.50 t (4H)	1.65 s (12H)	30.2, 41.3, 65.6, 66.4	113.7, 114.4, 125.6, 127.3, 130.9, 131.6, 142.9, 147.3, 155.5, 161.0	195.1
6	6.78, 7.68 dd (8H, J = 8.8 Hz), 6.97, 7.12 dd (8H, J = 8.8 Hz), 7.07 s (4H)	2.24 q (4H), 4.08 t (4H), 4.31 t (4H)	1.63 s (12H)	29.1, 30.9, 41.8, 63.5, 64.7	113.7, 114.3, 126.1, 127.7, 131.0, 132.2, 142.8, 147.9, 156.7, 162.2	195.3
7	6.78, 7.74 dd (8H, J = 8.6 Hz), 6.92, 7.14 dd (8H, J = 8.7 Hz), 7.11 s (4H)	2.01 m (8H), 4.02 t (4H), 4.18 t (4H)	1.63 s (12H)	25.6, 25.9, 31.0, 41.8, 67.3, 67.6	113.7, 114.0, 126.2, 127.7, 130.7, 132.2, 142.8, 147.8, 156.6, 162.0	194.8

Table 1 (continuation)

8	6.75, 7.70 dd (8H, J = 8.8 Hz), 6.91, 7.10 dd (8H, J = 8.8 Hz), 7.08 s (4H)	1.81 m (4H), 1.61 m (4H), 3.94 t (4H), 4.11 t (4H)	1.61 s (12H)	22.1, 27.6, 28.2, 30.4, 41.3, 67.1, 67.3	113.2, 113.6, 125.7, 127.2, 130.2, 131.7, 142.3, 147.3, 156.3, 161.7	194.5
9	6.83, 7.13 dd (8H, J = 8.8 Hz), 7.10 s (4H), 6.92 m (8H)	3.84 t (4H), 4.13 t (4H), 4.31 bs (8H)	1.66 s (12H)	30.8, 41.9, 66.8, 67.6, 68.7, 70.1	113.9, 114.2, 115.3, 121.7, 121.9, 126.4, 127.9, 143.4, 148.1, 148.8, 149.2, 156.7	
10	6.75, 7.12 dd (8H, J = 8.8 Hz), 7.62 d (2H), 6.96–7.1 m (4H), 7.05 s (4H)	3.98 t (4H), 4.12 t (4H), 2.03 m (8H)	1.64 s (12H)	24.9, 25.2, 30.8, 41.8, 66.2, 66.3	105.7, 113.8, 116.7, 126.1, 126.3, 127.8, 129.1, 135.9, 142.7, 148.1, 156.8, 157.5	

distinct shift in carbonyl group vibration towards longer wavelength. For related compounds **5–8** the greatest differences in band location occur for ν_{C-O-C} vibrations (1250–1230 cm^{-1} and 1120–1060 cm^{-1}). The smallest changes take place at *ca*. 1600 cm^{-1}, 1508 cm^{-1}, 1362 cm^{-1} and 925 cm^{-1}, corresponding to ν and δ vibrations of aromatic rings. The characteristic vibrations of macrocycles **5**–**10** are those of the aromatic rings, occurring at: ν_{C-C} = 1600–1610 cm^{-1}, 1576–1580 cm^{-1}, 1507–1513 cm^{-1}, 1360–1363 cm^{-1} and δ_{CHarom} = 828–852 cm^{-1}. The ether fragments yield intensive ν_{C-O-C} bands in the ranges 1245–1250, 1084–1093 and 1008–1030 cm^{-1}. Symmetrical vibrations of methylene groups (δ_{CH}) occur in the range 1470–1478 cm^{-1}. The remaining bands appearing in the IR spectra are listed in Table 2.

In the Raman spectra, the characteristic vibrations of compounds **5–8** are those of carbonyl groups occurring at 1657, 1649, 1637 and 1640 cm^{-1}, respectively. These vibrations appear in the same positions as in the IR spectra. For benzophenone and a model compound (4,4′-diethoxybenzophenone) these vibrations occur at 1652 and 1638 cm^{-1} [1]. Very strong C–C stretching vibrations occur for all compounds at *ca*. 1600 cm^{-1} . Other strong bands appearing for all compounds are those arising from scissor vibrations δ_{CH} of CH_2 fragments in the range 1450–1460 cm^{-1} and the stretching bands C–O–C occurring between 1160–1185 cm^{-1} and 1103–1109 cm^{-1}. In all Raman spectra there is a narrow band at 637–641 cm^{-1} that is absent from the IR spectra. This band probably originates in the framework of the molecules.

UV spectra: Table 4 shows UV bands as recorded in cyclohexane solution. A longer-wave absorption (250–300 nm) for model compound **20** (4,4′-diethoxybenzophenone) consists of three bands, not well resolved, reflecting $\pi \rightarrow \pi^*$ transitions and one band at λ = 225 nm with lower intensity. In the UV spectrum of tetraoxycyclophane **21** in cyclohexane the band intensity at λ = 224 nm is considerably greater and the long-wave segment of the spectrum contains a single wide band with λ_{max} = 276 nm. Combination of two benzophenone fragments "smoothes" the long-wave part of the spectrum resulting in the disappearance of its vibrational structure. UV spectra of model compounds **2–4** feature two distinct bands in the long-wave portion of the spectrum (λ = 278 and 285 nm) and one much stronger band at λ = 229 nm ($\varepsilon_{229}/\varepsilon_{278} \sim 6.5$). The combination of an aromatic fragment, as occurring in **2–4,** with a benzophenone fragment increases the intensity of all long-wave bands in compounds **5–8** and causes slight shift of the former. Also, the intensity of the λ = 225 nm band is lowered for the triphenyl fragment ($\varepsilon_{225}/\varepsilon_{277} \sim 1.8$). A similar spectrum is obtained when equimolar solutions of compounds **2** and **20** ($\varepsilon_{225}/\varepsilon_{278} = 1.64$) are mixed. The lack of bands reflecting $n \rightarrow \pi$-type transitions may be explained by their shift towards shorter wavelengths. The shoulder occurring at λ ~291 nm is probably related to the benzophenone part of the spectrum (its intensity is too great for bands of $n \rightarrow \pi$-type transitions). The UV spectrum of compound **10** is very similar to the spectrum of model compounds **2–4**. The effect on the spectrum of the two remaining phenyl fragments, separated by a considerable distance, remains minor. It is the triphenyl fragment that exerts a dominating effect upon the spectrum of compound **10.** The UV spectrum of compound **9** contains two additional bands at λ = 311 and 325

Table 2. The IR spectra for compounds **1–10**.

1	2	3	4	5	6	7	8	9	10
3602 s ~3279 s									
	3086 w 3060 w		3077 w 3044 w	3041 w	3039 w	3042 w	3044 w	3065 w	3057 w
3025 w	3030 w	3031 w	3026 w					3047 w	3034 w
		2983 s							
2967 s	2970 s	2968 s	2971 s	2962 s	2965 s	2964 vs	2961 s	2967 s	2964 s
	2928 s	2938 s	2934 s	2939 w	2934 w	2934 s	2942 s	2935 s	2930 s
	2907 s	2908 w	2905 s	2910 w			2907 sh		2910 w
2870 w	2872 s	2875 s	2869 s	2871 w	2872 w	2870 s	2870 s	2880 s	2870 w
				1657 s	1649 s	1637 s	1640 s		1630 s
1613 s	1609 s	1606 s	1607 vs	1602 vs	1601 vs	1600 vs	1601 vs	1610 s	1608 s
1596 vs	1604 s							1592 s	
	1579 s	1577 w	1578 s	1578 s	1577 w	1578 s	1576 s		1580 w
1512 vs	1508 vs	1510 vs	1513 vs	1508 vs	1509 vs	1510 vs	1508 vs	1507 vs	1511 vs
	1478 s	1475 s	1474 sh	1476 s	1470 s	1474 s	1473 s	1476 w	1472 w
		1460 w	1466 s	1459 w			1463 sh	1455 s	1459 w
1447 s	1439 s	1446 w		1418 w	1418 w	1417 w	1419 w		
1401 w	1391 s	1391 s	1393 s	1402 w	1400 w	1400 w	1399 w	1401 w	
1371 sh	1381 s			1384 w	1383 w	1385 w	1382 w	1377 w	1385 s
1361 s	1360 s	1361 w	1363 s	1363 w	1361 w	1362 w	1361 w	1362 w	1361 w
1300 w	1299 vs	1309 w		1305 s	1304 s	1305 s	1304 s	1330 w	1336 w
		1283 w	1288 s	1286 s	1283 s	1287 s	1285 s	1289 w	1296 w
				1262 s					
1245 vs	1245 vs	1247 vs	1247 vs	1243 vs	1250 vs	1248 s	1251 vs	1250 vs	1250 vs
1210 s	1227 vs	1232 s		1230 sh			1237 sh	1223 s	1210 vs

Table 2 (continuation)

1179 s	1182 vs	1179 s	1183 vs	1187 s	1183 s	1183 s	1182 s	1187 s	1182 s
				1171 s	1167 s	1168 s	1167 s		
	1158 s	1153 w	1145 w	1153 s	1150 w	1148 w	1146 s		1137 w
1122 w	1118 s	1122 w	1121 w			1120 w		1126 s	1118 w
1112 w				1109 w	1114 w	1108 w	1108 w		
1102 w		1106 w	1107 w						
1086 w	1085 s	1084 w	1086 w	1093 w		1087 w	1090 w	1093 w	1090 w
			1072 w	1069 w		1071 w	1072 w		1071 w
	1048 vs	1048 s	1042 s	1042 s	1054 s		1049	1053 w	
1013 s	1017 s	1022 s	1028 w	1027 w	1030 w	1037 s	1023 s	1038 w	
	1009 s	1008 sh	1012 s	1015 w	1013 w	1014 s	1014 s	1014 w	1018 s
			973 s		991 w	996 w		994 s	963 w
933 w	924 s	917 w		925 s	927 s	927 w	926 s	926 sh	919 w
912 w		903 w	909 w						
			874 w	850 s	851 w	847 w	852 w	839 s	854 w
829 vs	830 vs	830 vs	831 vs	832 s	831 s	832 s	828 s		829 vs
		816 w						810 w	
	801 s		803 w				805 w		
		767 w	764 w	768 s	769 s	768 s	769 s	784 w	766 w
754 w	753 s	756 w							748 w
725 w	731 w	729 w	742 w		730 w	730 w	728 w	735 s	729 w
688 w				688 w	686 w	685 w	683 w	698 w	
643 w	632 w	644 w	632 w		628 w	629 w	631 w		630 w
620 w				623 w			618 w		
586 s	594 vs	595 s	581 s	591 s	601 w	591 w	587 w	583 w	596 w
547 s	548 s	548 s	564 s		559 w	565 w	554 w	565 w	554 w
540 w			529 w					532 w	531 w

Table 3. Raman spectra of compounds **1–10**.

1	2	3	4	5	6	7	8	9	10
3066 s	3062 vs	3074 s	3074 s	3066 s	3066 s	3067 s	3068 s	3073 s	3066 s
		3044 s	3058 vs						
	2981 vs								
2972 s	2974 s	2970 vs	2974 vs	2970 w		2969 w	2966 w	2976 s	2966 s
	2929 s	2938 s	2934 sh	2928 w	2931 w	2934 w	2927 s	2931 s	2928
2916 w	2910 s	2910 s	2910 vs	2910 w		2911 sh	2909 w	2890 s	2920 s
2871 w	2875 w	2872 s	2869 vs		2871 w	2872 w	2869 w	2839 w	2871 s
				1656 s	1649 s	1636 s	1640 s		1629 w
1610 vs	1608 vs	1607 vs	1607 vs	1601 vs	1600 vs	1597 vs	1601 vs	1609 s	1609 s
1600 sh								1592 s	
	1580 w	1577 s	1579 w	1576 w	1577 w	1574 w	1574 s		
1495 w									
	1479 w							1479 w	1469 s
1462 s	1458 s	1464 s	1455 s	1461 w		1455 w		1459 s	1460 s
	1448 s	1448 s							1387 vs
						1330 w			
	1299 s		1299 w	1296 w	1294 w	1289 w	1311 w		
				1282 w			1283 w	1288 w	1296 w
1261 s			1249 w		1246 w	1251 w		1260 w	
	1228 s	1229 s				1223 w			1221 w
1213 s			1217 s	1215 w	1217 w				
			1200 s					1200 w	1201 w
1181 s	1182 s	1180 s	1184 s	1186 w		1183	1184 w	1163 w	1183 w
1140 s	1149 w		1146 w	1153 vs	1150 vs	1147 vs	1147 vs		
1105 vs	1109 s	1106 vs	1109 vs	1105 w	1108 w	1109 w	1103 w	1106 s	1105 s
	1081 w		1077 w				1076 w	1073 w	

Table 3 (continuation)

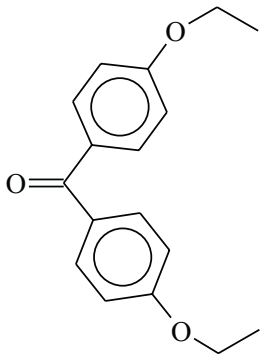
1009 s		1022 s						1053 w	
1003 s						1009 w			
923 s	927 w		911 w				929 w	937 w	
878 s									
845 vs		844 s	845 w	845 w	833 w			838 w	
	821 s	873 s	822 w	819 w	826 w	838 w	835 w		
	808 s			808 w		809 s		818 w	819 w
799 vs	792 vs	797 s	796 vs	788 w	800 w	796 s	781 w	794 vs	793 s
									780 vs
691 vs	697 vs	698 vs	698 vs	692 w	697 w	693 w		700 s	696 s
641 vs	637 s	640 s	641 s	640 w	639 w	641 s	640 s	641 s	640 s
596 s								596 w	
572 s		572 s							
545 s								536 w	

nm, which reflect $\pi \rightarrow \pi^*$ transitions in the naphthalene fragment. They have the smallest intensity ($\varepsilon = 2800$) but are nonetheless 10 times as intense as the corresponding bands in the spectrum of naphthalene itself ($\varepsilon = 290$). The comparison of band intensity at $\lambda = 277$ and 226 nm reveals a distinct increase of the latter ($\varepsilon_{226}/\varepsilon_{277} = 10.7$).

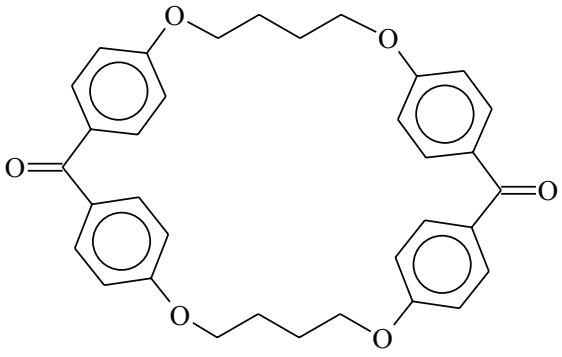
Table 4. UV spectra of compounds **2** to **10** and related compounds in cyclohexane solutions.

	λ(log ε)					$\varepsilon_a/\varepsilon_b$ *)
2	229 (4.43)	278 (3.62)	285 (3.55)			6.49
3	229 (4.45)	278 (3.63)	285 (3.56)			6.66
4	229 (4.49)	278 (3.68)	285 (3.62)			6.46
5	225 (4.69)	276 (4.42)	284 (4.39)			1.86
6	225.5 (4.69)	277.5 (4.42)	283.5 (4.40)			1.87
7	225 (4.61)	277 (4.33)	284 (4.31)			1.92
8	225.5 (4.64)	278.5 (4.42)	284.5 (4.41)			1.68
9	231 (4.91)	277.5 (3.88)	284.5 (3.83)	311 (3.45)	325 (3.62)	10.7
10	226.5 (4.62)	277.5 (3.99)	283.5 (3.88)			4.25
20	225		283	291.5		0.78
21	224	276				1.45
2 + 20	225.5	278.5	285	291.5		1.64

*) $\varepsilon_a/\varepsilon_b = \varepsilon_{\sim 255\ nm}/\varepsilon_{\sim 278\ nm}$.



20



21

Figure 6.

Crystallography: The structure of compound **3** is shown in Fig. 7. The molecule possesses crystallographic inversion symmetry with an interplanar angle of 88°. The side chains display an extended conformation. Numerous compounds are known to form clathrate combinations with neutral molecules [2,4–7]. Compounds synthesized by us also have the capacity to form clathrate-type combinations. They lack the possibility of direct chemical interaction between molecules. The presence of O heteroatoms in the macrocycle makes them potentially capable of efficient complex formation through hydrogen bonding with other uncharged molecules. Unfortunately, we have so far not been able to obtain crystals suitable for X-ray investigation from polar solvents containing hydrogen bond donors. The crystal structure of compound **5** was reported in [5]. Its molecular structure is based upon benzophenone and α,α′-diphenylene-1,4-diisopropylene units. The compound crystallizes from *para*-xylene with inclusion of solvent molecules. The molecular ratio of the solvent to phane molecules (3:2) was confirmed by ^{1}H NMR and thermogravimetric measurements, and by single crystal X-ray structural analysis. Of the three guest molecules, one is located between the two phane molecules and the other two are located in the crystal lattice between the complexes. Solvent-containing crystals suitable for X-ray studies were also obtained for compound **7** from *para*-xylene solution. Crystal data and molecular dimensions are given in Tables 5 and 7. Fig. 10 presents the crystallographic structure of the unit cell contents for the inclusion compound between **7** and *para*-xylene. Both ^{1}H NMR and crystallographic studies demonstrate that in this case molar ratio of solvent to phane molecules is 1:2. The guest molecule is surrounded by two host molecules and such a system, with crystallographic inversion symmetry, represents the unit cell contents; the asymmetric unit consists of one host and half a guest molecule. The cyclophane molecule is almost flat and its inner cavity is quite large (the dimensions are difficult to define precisely, but some idea is given by the interatomic distance H12...H12′, 5.9 Å and the intercentroid distance C44-49 to C44′-49′ 11.5 Å). The interplanar angle between the aromatic rings C7-12 and C14-19 is 50° (compared to 49° and 53° for two independent molecules of **20** [1] and 58° for compound **5** [5]). The shortest H...H distances between "host" molecules and those of the *para*-xylene "guest" are from H52C to H31 (2.69 Å), H4B′ (2.67 Å) and H5A′ (2.72 Å). Additionally, the contact from H12 to the centroid of the xylene ring (2.96 Å, angle at H12 161°) might be considered as a C–H...π hydrogen bond. Some weak contacts between neighbouring host-guest complexes could be classified as hydrogen bonds of the type C–H...O; the shortest is H31...O50, with H...O 2.65 Å, C–H...O 150°. The positioning of tetraoxacyclophane rings is alternate; the benzophenone fragment of one molecule faces the triphenyl fragment of the second tetraoxacyclophane molecule. Such positioning of phane molecules assures their better spatial "packing". In solution this clathrate system dissociates completely. Attempts to obtain single crystals of other tetraoxacyclophanes continue.

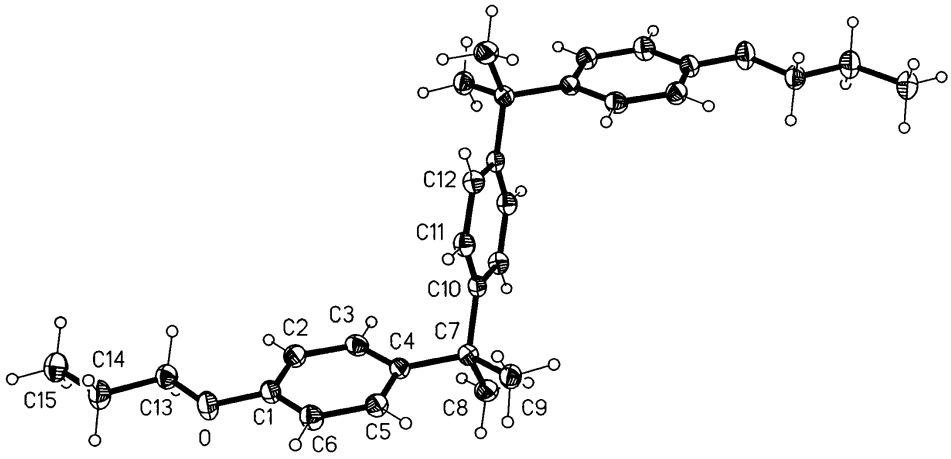


Figure 7. Schematic drawing of compound **3**.

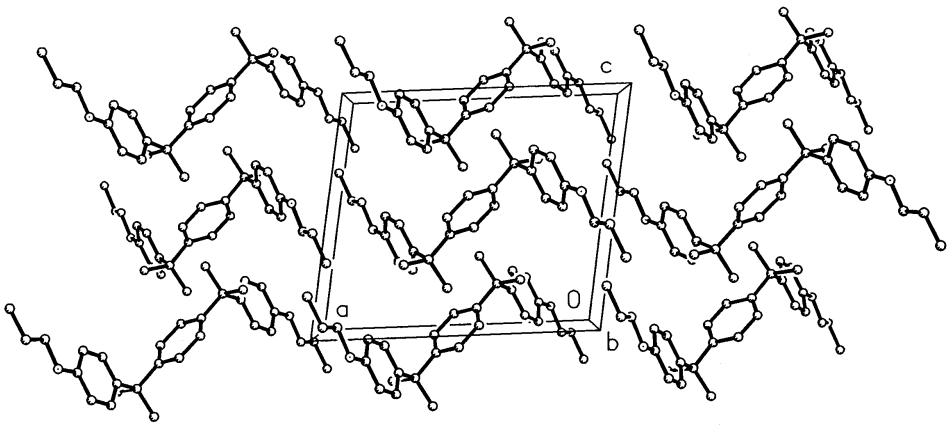


Figure 8. Packing diagram for compound **3**.

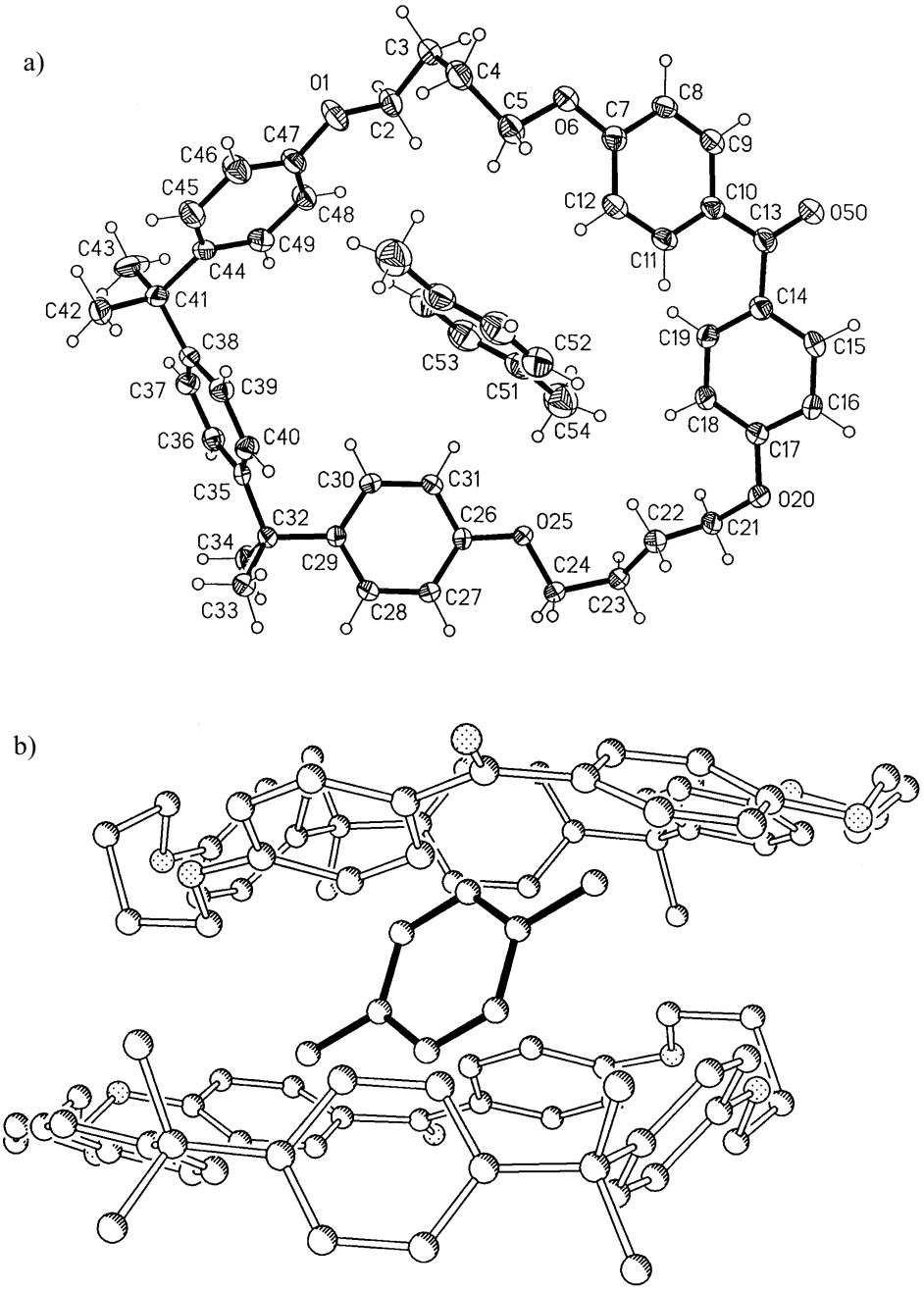


Figure 9. a) View of the host molecule **7** projected onto its least-square plane; b) Side view of the guest *para*-xylene molecule in the cavity formed by two host molecules.

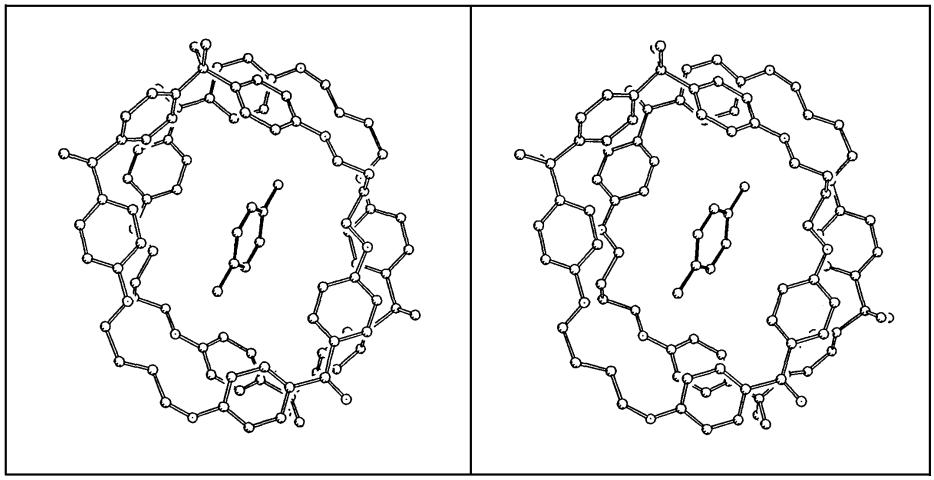


Figure 10. Packing diagram for compound **7**.

Table 5. Crystallographic data and refinement details for **3** and **7**.

	3	**7**
Compound	$C_{30}H_{38}O_2$	$C_{49}H_{53}O_5$
Formula weight	430.60	721.91
Crystal size/mm	0.70×0.50×0.20	0.50×0.40×0.25
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P(-1)$
Unit cell dimensions:		
a/Å	12.831(4)	10.506(2)
b/Å	8.708(2)	14.770(2)
c/Å	11.221(3)	14.917(2)
α/°	90	111.91(2)
β/°	99.20(3)	108.75(2)
γ/°	90	95.30(2)
Volume/Å^3	1237.6(6)	1973.3(5)
Z	2	2
Density/Mg m^{-3}	1.156	1.215

Table 5 (continuation)

Absorption coefficient/mm^{-1}	0.070	0.077
Temperature/K	143	153
Wavelength(MoKα)/Å	0.71073	0.71073
θ range/°	3.22 to 27.54	1.53 to 26.37
Limiting indices	–16 ≤ h ≤ 16	–13 ≤ h ≤ 12
	–1 ≤ k ≤ 11	–18 ≤ k ≤ 17
	0 ≤ l ≤ 14	0 ≤ l ≤ 18
F(000)	468	774
Reflections collected	3378	27335
Independent reflect. (R_{int})	2854 (0.0148)	8036 (0.0667)
Parameters	148	492
Goodness-of-fit on F^2	1.047	0.949
R1, *w*R2 [$I > 2\sigma(I)$]	0.0496, 0.1109	0.0411, 0.0956
R1, *w*R2 [all data]	0.0665, 0.1245	0.0645, 0.1053
Largest diff.peak and hole/e Å^{-3}	0.257 and –0.216	0.222 and –0.210

Table 6. Bond lengths [Å] and angles [°] for **3**.

O–C(1)	1.373(2)	O–C(13)	1.429(2)
C(1)–C(2)	1.389(2)	C(1)–C(6)	1.389(2)
C(2)–C(3)	1.388(2)	C(3)–C(4)	1.394(2)
C(4)–C(5)	1.393(2)	C(4)–C(7)	1.536(2)
C(5)–C(6)	1.388(2)	C(7)–C(10)	1.532(2)
C(7)–C(8)	1.534(2)	C(7)–C(9)	1.538(2)
C(10)–C(11)	1.395(2)	C(10)–C(12)#1	1.395(2)
C(11)–C(12)	1.388(2)	C(13)–C(14)	1.507(2)
C(14)–C(15)	1.522(2)		
C(1)–O–C(13)	117.69(11)	O–C(1)–C(2)	124.68(13)
O–C(1)–C(6)	116.13(13)	C(2)–C(1)–C(6)	119.20(13)
C(3)–C(2)–C(1)	119.56(13)	C(2)–C(3)–C(4)	122.28(13)
C(5)–C(4)–C(3)	117.07(13)	C(5)–C(4)–C(7)	123.37(12)
C(3)–C(4)–C(7)	119.52(12)	C(6)–C(5)–C(4)	121.40(13)
C(5)–C(6)–C(1)	120.46(14)	C(10)–C(7)–C(8)	112.09(12)
C(10)–C(7)–C(4)	109.15(11)	C(8)–C(7)–C(4)	108.19(11)
C(10)–C(7)-C(9)	108.25(11)	C(8)–C(7)–C(9)	107.26(12)
C(4)–C(7)–C(9)	111.93(12)	C(11)–C(10)–C(12)#1	116.67(13)
C(11)–C(10)–C(7)	119.64(13)	C(12)#1–C(10)–C(7)	123.67(13)
C(12)–C(11)–C(10)	122.25(13)	C(11)–C(12)–C(10)#1	121.07(13)
O–C(13)–C(14)	108.26(13)	C(13)–C(14)–C(15)	110.82(14)

Symmetry transformations used to generate equivalent atoms: #1 –x + 1, –y, –z + 1.

Table 7. Bond lengths [Å] and angles [°] for **7**.

O(1)–C(47)	1.367(2)	O(1)–C(2)	1.428(2)
C(2)–C(3)	1.504(2)	C(3)–C(4)	1.515(2)
C(4)–C(5)	1.501(2)	C(5)–O(6)	1.443(2)
O(6)–C(7)	1.356(2)	C(7)–C(12)	1.379(2)
C(7)–C(8)	1.392(2)	C(8)–C(9)	1.368(2)
C(9)–C(10)	1.384(2)	C(10)–C(11)	1.393(2)
C(10)–C(13)	1.492(2)	C(11)–C(12)	1.383(2)
C(13)–O(50)	1.226(2)	C(13)–C(14)	1.474(2)
C(14)–C(19)	1.388(2)	C(14)–C(15)	1.394(2)
C(15)–C(16)	1.364(2)	C(16)–C(17)	1.391(2)
C(17)–O(20)	1.352(2)	C(17)–C(18)	1.387(2)
C(18)–C(19)	1.371(2)	O(20)–C(21)	1.436(2)
C(21)–C(22)	1.518(2)	C(22)–C(23)	1.523(2)
C(23)–C(24)	1.510(2)	C(24)–O(25)	1.430(2)
O(25)–C(26)	1.380(2)	C(26)–C(27)	1.379(2)
C(26)–C(31)	1.380(2)	C(27)–C(28)	1.388(2)
C(28)–C(29)	1.385(2)	C(29)–C(30)	1.382(2)
C(29)–C(32)	1.543(2)	C(30)–C(31)	1.391(2)
C(32)–C(35)	1.521(2)	C(32)–C(34)	1.531(2)
C(32)–C(33)	1.535(2)	C(35)–C(36)	1.378(2)
C(35)–C(40)	1.391(2)	C(36)–C(37)	1.382(2)
C(37)–C(38)	1.378(2)	C(38)–C(39)	1.393(2)
C(38)–C(41)	1.521(2)	C(39)–C(40)	1.367(2)
C(41)–C(43)	1.529(2)	C(41)–C(44)	1.532(2)
C(41)–C(42)	1.537(2)	C(44)–C(45)	1.381(2)
C(44)–C(49)	1.385(2)	C(45)–C(46)	1.379(2)
C(46)–C(47)	1.382(2)	C(47)–C(48)	1.380(2)
C(48)–C(49)	1.386(2)	C(51)–C(52)	1.378(2)
C(51)–C(53)	1.386(2)	C(51)–C(54)	1.503(2)
C(52)–C(53)#1	1.378(2)		
C(47)–O(1)–C(2)	118.50(11)	O(1)–C(2)–C(3)	106.57(12)
C(2)–C(3)–C(4)	114.34(13)	C(5)–C(4)–C(3)	114.91(13)
O(6)–C(5)–C(4)	107.74(12)	C(7)–O(6)–C(5)	118.40(11)
O(6)–C(7)–C(12)	124.84(13)	O(6)–C(7)–C(8)	115.93(12)
C(12)–C(7)–C(8)	119.23(13)	C(9)–C(8)–C(7)	120.98(13)
C(8)–C(9)–C(10)	120.96(14)	C(9)–C(10)–C(11)	117.42(13)
C(9)–C(10)–C(13)	118.34(13)	C(11)–C(10)–C(13)	124.15(13)
C(12)–C(11)–C(10)	122.32(13)	C(7)–C(12)–C(11)	119.03(13)
O(50)–C(13)–C(14)	119.29(13)	O(50)–C(13)–C(10)	120.69(13)
C(14)–C(13)–C(10)	120.00(13)	C(19)–C(14)–C(15)	118.52(13)
C(19)–C(14)–C(13)	122.99(13)	C(15)–C(14)–C(13)	118.47(13)
C(16)–C(15)–C(14)	120.52(13)	C(15)–C(16)–C(17)	120.06(14)
O(20)–C(17)–C(18)	124.55(13)	O(20)–C(17)–C(16)	115.24(13)

Table 7 (continuation)

C(18)–C(17)–C(16)	120.21(13)	C(19)–C(18)–C(17)	118.88(13)
C(18)–C(19)–C(14)	121.60(13)	C(17)–O(20)–C(21)	118.83(11)
O(20)–C(21)–C(22)	116.32(12)	C(21)–C(22)–C(23)	107.89(11)
C(24)–C(23)–C(22)	116.79(12)	O(25)–C(24)–C(23)	109.09(11)
C(26)–O(25)–C(24)	117.16(10)	C(27)–C(26)–O(25)	124.80(12)
C(27)–C(26)–C(31)	118.32(12)	O(25)–C(26)–C(31)	116.88(12)
C(26)–C(27)–C(28)	120.10(13)	C(29)–C(28)–C(27)	122.76(13)
C(30)–C(29)–C(28)	116.08(12)	C(30)–C(29)–C(32)	123.54(12)
C(28)–C(29)–C(32)	120.35(12)	C(29)–C(30)–C(31)	122.02(13)
C(26)–C(31)–C(30)	120.71(13)	C(35)–C(32)–C(34)	110.90(11)
C(35)–C(32)–C(33)	108.55(11)	C(34)–C(32)–C(33)	107.45(12)
C(35)–C(32)–C(29)	111.66(11)	C(34)–C(32)–C(29)	108.67(11)
C(33)–C(32)–C(29)	109.51(11)	C(36)–C(35)–C(40)	116.87(12)
C(36)–C(35)–C(32)	123.39(12)	C(40)–C(35)–C(32)	119.74(12)
C(35)–C(36)–C(37)	122.13(13)	C(38)–C(37)–C(36)	120.77(13)
C(37)–C(38)–C(39)	117.24(12)	C(37)–C(38)–C(41)	123.62(13)
C(39)–C(38)–C(41)	119.05(12)	C(40)–C(39)–C(38)	121.70(13)
C(39)–C(40)–C(35)	121.21(13)	C(38)–C(41)–C(43)	112.28(13)
C(38)–C(41)–C(44)	108.95(11)	C(43)–C(41)–C(44)	108.30(12)
C(38)–C(41)–C(42)	107.30(12)	C(43)–C(41)–C(42)	107.89(14)
C(44)–C(41)–C(42)	112.17(13)	C(45)–C(44)–C(49)	116.95(13)
C(45)–C(44)–C(41)	122.79(13)	C(49)–C(44)–C(41)	120.23(13)
C(46)–C(45)–C(44)	121.43(14)	C(45)–C(46)–C(47)	120.57(14)
O(1)–C(47)–C(48)	124.67(13)	O(1)–C(47)–C(46)	115.91(13)
C(48)–C(47)–C(46)	119.42(13)	C(47)–C(48)–C(49)	118.93(14)
C(44)–C(49)–C(48)	122.70(14)	C(52)–C(51)–C(53)	117.6(2)
C(52)–C(51)–C(54)	121.1(2)	C(53)–C(51)–C(54)	121.3(2)
C(51)–C(52)–C(53)#1	121.2(2)	C(52)#1–C(53)–C(51)	121.2(2)

Symmetry transformation used to generate equivalent atoms: #1 –x + 2, –y, –z.

EXPERIMENTAL

4,4′-Dihydroxybenzophenone was purchased from Aldrich Chemical Co. and used as received. α,α′-Bis(4-hydroxyphenyl)-1,4-diisopropylbenzene was synthesized as described in [3]. 4,4′-Di-(2-bromo-1-ethoxy)benzophenone (**11**), 4,4′-di-(3-bromo-1-propoxy)benzophenone (**12**), and 4,4′-di-(4-bromo-1-butoxy)benzophenone (**13**) were synthesized as described in [1]; 2,2′-(3-oxa-pentane-1,5-diyldioxy)-bis-phenol was synthesized according to the procedure described by Weber and Voegtle [8]. The proton NMR spectra were recorded with IBM AF200 and General Electric QE-300 spectrometers, chemical shifts are in ppm ($CDCl_3$/TMS). Electronic spectra were recorded on a JASCO V-530 spectrophotometer in cyclohexane solutions. The IR spectra were recorded with the Perkin Elmer Spectrum One FT-IR spectrometer in KBr pellets. The Raman spectra were measured using the Raman accessory with the Nicolet FT-IR Magna 560 spectrometer (Nd:WVO_4 laser worked in the near infrared range (9600 cm^{-1})). Mass spectrometry was performed on a LSIMS(+) model AMD 604 (AMD Intectra) spectrometer (NBA matrix). ESI mass spectra were recorded on API 365 (Perkin-Elmer-Sciex) triple quadrupole mass spectrometer. All calculations were performed with HyperChem 5.0 (Hypercube Inc.,

Waterloo, Ontario Canada) using common its techniques. Colourless single crystals of **3** and **7** were obtained from *para*-xylene solutions by slow evaporation. Data were recorded on a Stoe STADI-4 (**3**) or a Bruker SMART 1000 CCD diffractometer (**7**). Structures were solved by direct methods and refined anisotropically against F^2; hydrogen atoms were included using a riding model or rigid methyl groups. Further crystallographic, experimental and computational details are given in Table 5. Program used to solve structures: SHELXS-86 [9]. Program used to refine structures: SHELXL-93 [10]. Molecular graphics: Siemens XP [11].

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC-140692 for **3** and CCDC-140693 for **7**. Copies can be obtained free of charge from CCDC, 12 Union Road. Cambridge CB2 1EZ, U.K. (Fax: Int.+1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

α,α′-Bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (1): ^{1}H NMR; δ ($CDCl_3$): 1.61 (s, 12H), 4.65 (s, 2H), 6.70, 7.08 (dd, 8H, J = 8.7 Hz), 7.07 (s, 4H).

General procedure for synthesis of di-alkyl derivatives of α,α′-bis-(4-hydroxy-phenyl)-1,4-diisopropylbenzene 2–4: A stirred solution of **1** (10 mmol), bromoalkyl derivative (*ca*. 80–100 mmol), and K_2CO_3 (5g, 36 mmol) in acetone (*ca*. 100 cm^3) was refluxed for 10–14 hours. The solvent was removed *in vacuo* (water pump). To the residue dichloromethane was added and the obtained mixture was washed a few times with water. The organic layer was dried with anhydrous $MgSO_4$ and then passed through a short silica gel column. The product was eluted as the first fraction. The crude compound was crystallized from dichloromethane/methanol.

α,α′-Bis(4-ethoxyphenyl)-1,4-diisopropylbenzene (2): yield 62%, m.p. 92–94°C; Found: C, 83.5; H, 8.62. Anal. calc. for $C_{28}H_{34}O_2$: C, 83.54; H, 8.51.

α,α′-Bis(4-propyloxyphenyl)-1,4-diisopropylbenzene (3): yield 55%, m.p. 86–87°C; Found: C, 83.61; H, 8.91. Anal. calc. for $C_{30}H_{38}O_2$: C, 83.67; H, 8.89. Colourless single crystals of compound **3** were obtained from a *para*-xylene solution by slow evaporation.

α,α′-Bis(4-butyloxyphenyl)-1,4-diisopropylbenzene (4): yield 38%, m.p. 95–97°C; Found: C, 83.52; H, 9.20. Anal. calc. for $C_{32}H_{42}O_2$: C, 83.79; H, 9.23.

General procedure for the synthesis of cyclophanes 5–10: A stirred solution of the dibromo-derivative (1.5 mmol), the dihydroxy-derivative (1.5 mmol), and Cs_2CO_3 (3 g) in DMF (50 cm^3) was heated at 60°C for 3–4 days, after which the solvent was removed *in vacuo*. Water was added to the residue and the mixture was extracted with dichloromethane. The extract was washed with water (three times) and dried with anhydrous $MgSO_4$. The crude product was chromatographed on a silica gel column with dichloromethane as eluent.

28,28,35,35-Tetramethyl-11-oxo-1,4,18,21-tetraoxa[4.1.4.1.1]paracyclophane (5): yield 29 %; m.p. 200–203°C (from dichloromethane). ESI-MS: 613 $[M+1]^+$. Found: C, 80.25; H, 6.62. Anal. calc. for $C_{41}H_{40}O_5$: C, 80.37; H, 6.58.

30,30,37,37-Tetramethyl-12-oxo-1,5,19,23-tetraoxa[5.1.5.1.1]paracyclophane (6): yield 26%; m.p. 102–105°C; LSIMS: 641 $(M.+1)^+$. Found: C, 80.82; H, 7.01. Anal. calc. for $C_{43}H_{44}O_5$: C, 80.60; H, 6.92.

32,32,39,39-Tetramethyl-13-oxo-1,6,20,25-tetraoxa[6.1.6.1.1]paracyclophane (7): yield 29%; m.p. 168–171°C (from dichloromethane after column chromatography); ESI-MS: 669 $(M.+1)^+$. Found: C, 80.9; H,7.2. Anal. calc. for $C_{45}H_{48}O_5$: C, 80.81; H, 7.23. Colourless single crystals of the host-guest complex were obtained from a *para*-xylene solution of **7** by slow evaporation.

34,34,41,41-Tetramethyl-14-oxo-1,7,21,27-tetraoxa[7.1.7.1.1]paracyclophane (8): yield 15%; m.p. 151–152°C; ESI-MS: 697 $(M.+1)^+$. Found: C, 81.5; H, 7.50. Anal. calc. for $C_{47}H_{52}O_5$: C, 81.00; H, 7.52.

34,34,41,41-Tetramethyl-1,4,11,14,17,24,27-heptaoxa[4.7]orthocyclo[4.1.1]paracyclophane (9): yield 22%, m.p. 173–174°C (from *p*-xylene), ESI-MS: 689 $(M.+1)^+$, EI: 688 $(M.^+)$. Found: C, 76.9; H, 7.14. Anal. calc. for $C_{44}H_{48}O_7$: C, 76.72; H, 7.02.

29,29,36,36-Tetramethyl-1,6,17,22-tetraoxa[6](2,7)naphthalene[6.1.1]paracyclophane (10): yield 16%, m.p. 148–151°C (from CH_2Cl_2/EtOAc), ESI-MS: 615 $(M.+1)^+$. Found: C, 82.4; H,7.7. Anal. calc. for $C_{42}H_{46}O_4$: C, 82.05; H, 7.54.

α,α′-Bis[(2-bromo-1-ethoxy)phenyl]-1,4-diisopropylbenzene (15): This compound was synthesized according to the procedure described in [2]. The crude product was chromatographed on silica gel

with mixture hexane:dichloromethane (1:1, v/v) as eluent. Three main fractions were separated. The first fraction was compound **15**. Yield 40–48%; m.p. 102–104°C. ^{1}H NMR δ ($CDCl_3$): 1.63 s (12H), 3.62 t (4H), 4.26 t (4H), 6.80, 7.14 dd (8H, J = 8.8 Hz), 7.09 s (4H), ^{13}C NMR: 29.2, 30.8, 41.8, 67.7, 113.9, 126.1, 127.8, 143.7, 147.7, 155.8. IR (KBr) cm^{-1}: 3061, 3043, 2969, 2929, 2904, 2870, 2856, 1609, 1580, 1507, 1451, 1420, 1384, 1363, 1291, 1248, 1188, 1077, 1016, 880, 827, 780, 570, 527. Found: C, 60.3; H, 5.7. Anal. calc. for $C_{28}H_{32}O_2Br_2$: C, 60.01; H, 5.75. The second fraction was **1,2-di [4-(4′-(4′′-(2-bromo-1-ethoxy)phenyl-1′′-isopropylene)-phenyl-1′-isopropylene)phenoxy]ethane (18)**. Yield 20–25% ; m.p. 168.5–170°C. ^{1}H NMR δ ($CDCl_3$): 7.15, 6.80 dd (8H, J =8 .8 Hz), 7.15, 6.83 dd (8H, J = 8.8 Hz), 7.12 s (8H), 4.25–4.35 m (4H), 4.26 t (4H), 3.62 t (4H), 1.63 s (24H). IR (KBr) cm^{-1}: 3045, 2969, 2931, 2873, 1607, 1581, 1510, 1479, 1457, 1401, 1384, 1362, 1295, 1247, 1184, 1106, 1076, 1052, 1030, 1015, 880, 832, 755, 581, 561, 529. The third fraction was **α-[(2-bromo-1-ethoxy)phenyl]-1,4-di-isopropylbenzene (19)**. Yield 3–5%; m.p. 66–68°C. ^{1}H NMR δ ($CDCl_3$): 7.14, 6.78 dd (4H, J = 8.8 Hz), 7.08, 6.71 dd (4H, J = 8.8 Hz), 7.08 s (4H), 4.62 s (1H), 4.24 t (2H), 3.61 t (2H), 1.62 s (12H). IR (KBr) cm^{-1}: 3589, 3391, 3272, 3086, 3049, 3027, 2968, 2930, 2873, 1610, 1597, 1510, 1455, 1385, 1297, 1248, 1182, 1090, 1026, 1015, 880, 833, 752, 660, 617, 588.

α,α′-Bis[(5-bromo-1-pentoxy)phenyl]-1,4-diisopropylbenzene (14) was synthesized by a similar method to the preparation of **15**. Yield: 65%; m.p. 86–88°C. ^{1}H NMR δ ($CDCl_3$): 1.63 s (12H), 1.65–2.00 m (12H), 3.44 t (4H), 3.95 t (4H), 6.78, 7.13 dd (8H, J = 8.8 Hz), 7.09 s (4H); IR (KBr) cm^{-1}: 3047, 3035, 2974, 2944, 2927, 2917, 2868, 1610, 1575, 1511, 1468, 1454, 1434, 1392, 1384, 1362, 1284, 1249, 1183, 1154, 1087, 1069, 1039, 960, 835, 813, 798, 754, 732, 596, 554. Found: C, 63.4; H, 6.78. Anal. calc. for $C_{34}H_{44}O_2Br_2$: C, 63.36; H, 6.88.

2,7-Di-(4-bromo-1-butoxy)naphthalene (**16**): A solution of 2,7-dihydroxynaphthalene (2 g, 12.5 mmol), 1,4-dibromobutane (20 g, 92.5 mmol), and K_2CO_3 (10 g, 72 mmol) in acetone (100 cm^3) was refluxed for 10 hrs. The solvent was removed *in vacuo* and to the residue dichloromethane and water were added. The organic layer was separated, washed with water and dried with anhydrous $MgSO_4$. The dried solution was chromatographed on a silica gel column with a mixture of dichloromethane and hexane (1:1, v/v). The first fraction was compound **16**. Yield: 1.74 g (32.4%); m.p. 78–79°C. ^{1}H NMR δ ($CDCl_3$): 7.64 d (2H), 6.94–7.05 m (4H), 4.09 t (4H), 3.51 t (4H), 1.9–2.3 m (8H); IR (KBr) cm^{-1}: 3026, 3000, 2948, 2910, 2869, 1626, 1604, 1514, 1454, 1386, 1278, 1255, 1210, 1181, 1147, 1048, 1011, 955, 866, 839, 825, 737. Found: C,50.2; H, 5.14. Anal.calc.for $C_{18}H_{22}O_2Br_2$: C,50.26; H, 5.15. The second fraction was **1,4-di-[7-(4-bromo-1-butoxy)-2-naphthyloxy]butane** (**17**). Yield: 0.11 g; m.p. 148–150°C. ^{1}H NMR δ ($CDCl_3$): 7.65 d (4H), 6.95–7.1 m (8H), 4.1–4.3 m (4H), 4.08 t (4H), 3.51 t (4H), 1.9–2.3 m (12H). IR (KBr) cm^{-1}: 3054, 3029, 2961, 2939, 2881, 2850, 1626, 1607, 1515, 1460, 1431, 1385, 1331, 1256, 1215, 1173, 1117, 1048, 997, 972, 928, 861, 835, 737, 631, 615, 553, 472.

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