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Cyclic Esters of Aliphatic Diacids with Pyrocatechol and Hydroquinone

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Cyclic esters of adipic acid, suberic acid and sebacic acid were prepared by reaction of the acid dichlorides and pyrocatechol or hydroquinone in benzene under high dilution conditions. While only the cyclic dimers could be obtained from hydroquinone, pyrocatechol formed cyclic monomers as well as cyclic dimers (and also a cyclic dimer with succinic acid). The structure of all compounds was confirmed by ^{1}H-NMR- and mass spectra. The crystal structures of the pyrocatechol esters were determined by single crystal X-ray analysis.

(Keywords: Cyclic monomers; Cyclic dimers; High dilution conditions; Crystal structure; Mass spectra)

Cyclische Ester aliphatischer Dicarbonsäuren mit Brenzcatechin und Hydrochinon

Es wurden cyclische Ester von Adipinsäure, Korksäure und Sebacinsäure durch Reaktion der entsprechenden Säure-Dichloride mit Brenzcatechin oder Hydrochinon bei hoher Verdünnung hergestellt. Während mit Hydrochinon lediglich die cyclischen Dimeren erhalten werden konnten, wurden mit Brenzcatechin sowohl cyclische Monomere als auch cyclische Dimere erhalten (ebenfalls das cyclische Dimer mit Bernsteinsäure). Die Strukturen wurden mittels ^{1}H-NMR und Massenspektren gesichert. Die Kristallstrukturen der Brenzcatechin-Ester wurden mittels Röntgenstrukturanalyse bestimmt.

Introduction

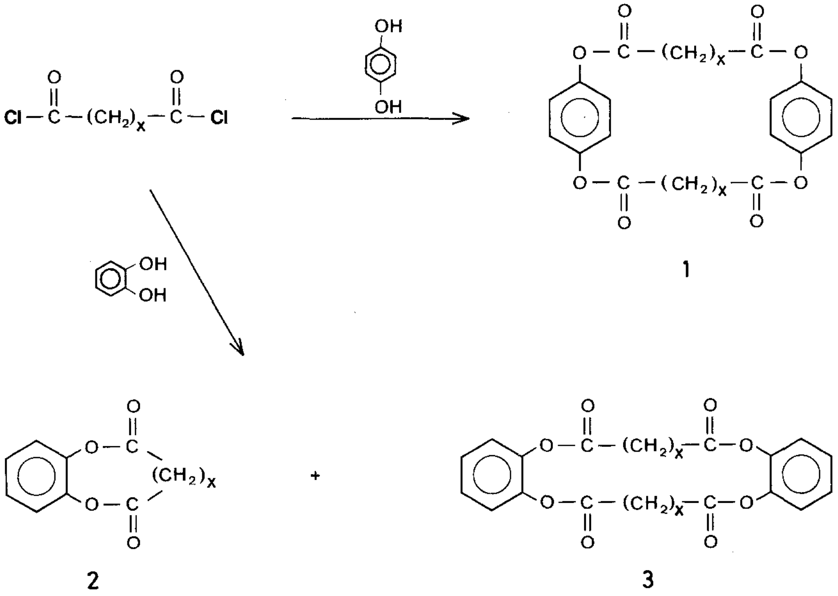
The *Fries* rearrangement of phenylesters[1,2] may be catalyzed by *Lewis* acids or initiated by UV-irridation. This photo-*Fries* reaction[3] is an intramolecular process[4] and thus, cyclic hydroxyketones should be obtained from cyclic esters of diphenols and dicarboxylic acids. However, deviations from the normal pathway could be caused for instance by steric reasons. Such an unusual reaction product was found, when *o*-phenylene oxalate was irridated to yield nearly exclusively *o*-phenylene carbonate by the loss of carbonmonoxide[5], while acyclic aryl oxalates undergo the usual photo-*Fries* rearrangement with the simultaneous formation of phenols[6]. Therefore, it would be interesting not only from a preparative, but also from a mechanistic point of view, to study the photo-*Fries* reaction of suitable cyclic esters.

Mainly for these purposes we synthesized some cyclic esters of pyrocatechol and hydroquinone with aliphatic dibasic acids. Although a lot of macrocyclic di- and tetraester compounds have been prepared by different methods[7], these comparatively simple compounds were unknown, until recently some similar esters[8] and thioesters[9] were described.

Results and Discussion

Synthesis and Properties

All esters were prepared under high dilution conditions in boiling benzene from stoechiometric amounts of pyrocatechol or hydroquinone and the diacid chloride. To neutralize the hydrogenchloride a stoechiometric quantity of triethylamine was applied in the case of pyrocatechol



and an excess of pyridine in the case of hydroquinone. These conditions were also chosen to get a sufficient solubility of the diphenol in benzene. After filtration of the amine hydrochloride the reaction mixture was evaporated and in general separated by column chromatography.

As indicated in the reaction scheme only dimeric compounds were obtained from hydroquinone and adipic, suberic, and sebacic acid ($x = 4$, 6, 8), while no definite reaction product could be isolated with succinic acid ($x = 2$). This result can be understood by steric hindrance, although molecule models show that a cyclic dimer should be possible also for $x = 2$, and a cyclic monomer at least for $x = 8$ and of course for longer diacids.

But obviously it is difficult or impossible for the ester groups to have the *s*-trans conformation of the aromatic residue and the aliphatic chain in these cases. [According to the IUPAC rule E-2.2.2. this is the (*Z*)-conformation.] This preferred conformation of normal esters was found for similar cyclic esters of the paracyclophane type[10], and it is assumed also for the cyclic monomers **2** and the cyclic dimers **3** in the solid state (see later).

Cyclic monomers are obtained from pyrocatechol and adipic, suberic and sebacic in 30–50% yield, but they are always accompanied by about 30% of the cyclic dimer. This dimer was the only product which could be identified in the reaction with succinic acid. Similar dimers (with $x = 3$, 5, 7, and also 8) were prepared in benzene without dilution from a cyclic antimony derivative of pyrocatechol (2-chloro-1,3,2-benzodioxastibole) and diacid dichlorides (18–43% yield)[8].

The formation of cyclic monomers was not observed under these conditions, and probably the dimers have in general a high tendency of formation, because **3** ($x = 8$) was obtained also at least to 5% from pyrocatechol and sebacic acid dichloride in benzene/triethylamine without dilution conditions. For a similar structural case—the reaction of α,α'-dibromo-*o*-xylene with aliphatic dicarboxylic acids—only the formation of cyclic dimers was reported as well[11].

Table 1 contains the yields of pure cyclic esters. The melting points of all esters, dimers as well as monomers decrease with increasing chain length of the dibasic acid, an effect which was also observed for the odd numbers $x = 3$, 5, and 7[8]. All spectral data are in accordance with the proposed structure. IR-spectra show the complete disappearance of hydroxyl groups and a carbonyl absorption around 1740–1765 cm^{-1} which is split into two peaks (1740 cm^{-1}, 1760 cm^{-1}) for the smallest cyclic monomer **2** ($x = 4$). ^{1}H-NMR spectra show mainly three groups of signals: Aromatic protons in the range of 7.1–7.25 ppm for hydroquinone esters (singulet) and 7.2–7.35 ppm for pyrocatechol esters (pseudo singulet), methylene protons adjacent to the carbonyl group as a triplet

Table 1. *Preparation of cyclic esters*

Compound	Yield (%)	Melting point (°C)	Recrystallized from
1 $x=4$	44	175–177	acetone or $CHCl_3$
1 $x=6$	51	138	$CHCl_3$
1 $x=8$	58	108–110	$CHCl_3$
2 $x=4$	32	163–164	$CHCl_3$/petroleum ether
2 $x=6$	49	90	$CHCl_3$/petroleum ether
2 $x=8$	44	54	petroleum ether
3 $x=2$	44	238–239	CH_2Cl_2
3 $x=4$	32	154	$CHCl_3$
3 $x=6$	30	126	$CHCl_3$/petroleum ether
3 $x=8$	31	124[a]	acetone

[a] Lit.[8] m.p. 108–110 °C.

Table 2. *Electron impact mass spectra of cyclic esters (Varian CH 7 a, 70 eV)*

Compound	*m*/e (intensity in %)	Temperature (°C)
1 $x=4$	440 (5), 330 (4), 221 (17), 210 (14), 196 (5), 111 (64), 110 (100)	275
1 $x=6$	496 (85), 387 (13), 358 (11), 249 (15), 139 (76), 111 (36), 110 (100)	185
1 $x=8$	552 (10), 443 (31), 333 (8), 277 (11), 240 (10), 167 (8), 110 (100)	300
2 $x=4$	220 (19), 111 (100), 110 (47)	240
2 $x=6$	248 (38), 139 (100), 121 (12), 110 (57)	70
2 $x=8$	276 (17), 167 (74), 149 (26), 139 (16), 121 (79), 110 (100)	55
3 $x=2$	384 (14), 275 (8), 247 (8), 193 (6), 147 (8), 111 (27), 110 (9), 55 (100)	130
3 $x=4$	440 (5), 331 (5), 221 (34), 203 (19), 111 (100), 110 (13)	155
3 $x=6$	496 (26), 387 (61), 277 (79), 249 (45), 139 (100), 110 (13)	170
3 $x=8$	552 (1), 443 (21), 333 (6), 276 (20), 167 (97), 149 (40), 139 (26), 121 (96), 110 (99), 55 (100)	85

around 2.55–2.7 ppm, and the further methylene protons as a multiplet between 1.45 and 2.0 ppm. For **3** ($x = 2$) the methylene protons are found as singulet at 3.05 ppm and the aromatic protons at 7.45 ppm.

Mass spectral data of the cyclic esters are collected in Table 2. All

Table 3. *Crystal data and results of refinements*

	2 ($x = 4$)	**2** ($x = 6$)	**2** ($x = 8$)	**3** ($x = 4$)	**3** ($x = 6$)	**3** ($x = 8$)
Molecular formula	$C_{12}H_{12}O_4$	$C_{14}H_{16}O_4$	$C_{16}H_{20}O_4$	$C_{24}H_{24}O_8$	$C_{28}H_{32}O_8$	$C_{32}H_{40}O_8$
Molecular weight	220.2	248.3	276.3	440.4	496.6	552.7
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_1/a$	$P\bar{1}$	Pbcn	$P2_1/a$	$P2_1/c$
a(Å)	13.098	9.610	12.050	16.429	16.216	20.192
b	5.601	22.784	8.933	12.165	5.504	5.418
c	15.700	5.809	8.034	10.810	14.127	15.355
α(°)	90	90	112.05	90	90	90
β	113.55	91.25	102.41	90	92.16	118.65
γ	90	90	102.25	90	90	90
V(Å^3)	1 055.9	1 271.6	741.2	2 160.5	1 260.0	1 474.2
Z	4	4	2	4	2	2
D_c(g/cm^3)	1.39	1.30	1.24	1.35	1.31	1.25
N_t[a]	1 540	1 901	1 928	1 598	1 867	2 071
N_0[b]	1 306	1 631	1 721	1 313	1 538	1 702
F_{max}, f[c]	10, 0.3	23, 0.06	15, 0.35	20, 0.19	20, 0.4	20, 0.33
Final R	0.063	0.118	0.109	0.050	0.050	0.054
Final ωR	0.082	0.103	0.127	0.070	0.067	0.071
N_e[d]	15	—	—	8	12	9

[a] Number of independent reflections measured.

[b] Number of significant reflections $[I > 2\sigma(I)]$.

[c] Weighting scheme used in the final cycle of the refinement in the form; $\omega = 1.0$ for $F_0 < F_{max}$ and $\omega = [1.0 + f(F_0 - F_{max})]^{-1}$ for $F_0 > F_{max}$.

[d] Number of reflections applied for extinction correction.

Table 4. *Final atomic coordinates of non hydrogen atoms with estimated standard deviations in parentheses for cyclic esters of pyrocatechol and adipic acid (x = 4)*

	cyclic monomer **2**			cyclic dimer **3**		
	x	*y*	*z*	*x*	*y*	*z*
C(1)	0.6383 (3)	0.2854 (6)	0.3197 (2)	0.1186 (2)	0.1755 (3)	0.1778 (3)
C(2)	0.6829 (3)	0.1065 (6)	0.3839 (2)	0.1361 (2)	0.0840 (3)	0.2479 (3)
C(3)	0.7955 (3)	0.1078 (6)	0.4381 (2)	0.2062 (2)	0.0824 (3)	0.3191 (3)
C(4)	0.8628 (3)	0.2874 (7)	0.4284 (2)	0.2576 (2)	0.1719 (3)	0.3210 (3)
C(5)	0.8176 (3)	0.4686 (6)	0.3632 (2)	0.2395 (2)	0.2636 (3)	0.2506 (3)
C(6)	0.7055 (2)	0.4646 (6)	0.3093 (2)	0.1697 (2)	0.2648 (2)	0.1787 (3)
C(7)	0.6143 (3)	0.6001 (6)	0.1539 (2)	0.1208 (2)	0.4474 (2)	0.1563 (2)
C(8)	0.4615 (3)	0.4663 (6)	0.2757 (2)	0.0435 (2)	0.1602 (2)	—0.0098 (3)
C(9)	0.5356 (3)	0.7903 (6)	0.0991 (2)	0.1231 (2)	0.5402 (2)	0.0658 (3)
C(10)	0.3528 (3)	0.4868 (7)	0.1944 (3)	—0.0426 (2)	0.1601 (2)	—0.0564 (3)
C(11)	0.4308 (3)	0.8061 (7)	0.1195 (3)	0.0699 (2)	0.6376 (2)	0.1017 (3)
C(12)	0.3670 (3)	0.5686 (7)	0.1071 (3)	—0.0926 (2)	0.2628 (3)	—0.0231 (3)
O(1)	0.6541 (2)	0.6495 (4)	0.2470 (1)	0.1534 (2)	0.3547 (2)	0.1026 (2)
O(2)	0.6388 (2)	0.4221 (5)	0.1246 (2)	0.0986 (2)	0.4490 (2)	0.2604 (2)
O(3)	0.5252 (2)	0.2867 (4)	0.2618 (1)	0.0448 (1)	0.1796 (2)	0.1147 (2)
O(4)	0.4951 (2)	0.5886 (5)	0.3436 (2)	0.1036 (1)	0.1425 (2)	—0.0663 (2)

compounds show a molecular ion peak which confirms the proposed structure. It has always its highest intensity for compounds with $x = 6$, however, a detailed comparison is difficult, because the spectra were taken at quite different temperatures. Fragmentation of the molecular ion occurs by cleavage of the ester bond (—CO—O—) and the acylcation may further split off carbon monoxide and ethylene. On the other hand the decomposition of the ester structure may lead to ketene and phenol. Thus, all peaks can be explained according to Ref.[12].

Crystal Structure

The structure of the cyclic monomers **2** and the corresponding cyclic dimers **3** with pyrocatechol was further confirmed by single crystal X-ray analysis. Unfortunately no suitable crystals could be obtained from **1**. The crystal data for all six compounds are listed in Table 3. Fractional atomic coordinates are given in Tables 4 to 6 and Table 7 contains selected bond lengths, bond angles and torsion angles*. To make a comparison of all compounds possible, the following general indication of the atoms is used

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* The atomic parameters of the hydrogen atoms, anisotropic temperature factors and observed and calculated structure factors are available from the authors (*K. F.*) on request.

Table 5. *Final atomic coordinates of non hydrogen atoms with estimated standard deviations in parentheses for cyclic esters of pyrocatechol and suberic acid ($x = 6$)*

	cyclic monomer **2**			cyclic dimer **3**		
	x	y	z	x	y	z
C(1)	0.6162 (6)	0.6615 (3)	0.1912 (11)	0.4033 (2)	0.3909 (5)	0.1246 (2)
C(2)	0.5675 (7)	0.6915 (3)	0.3785 (11)	0.4200 (2)	0.2264 (5)	0.0542 (2)
C(3)	0.4255 (8)	0.6913 (3)	0.4226 (12)	0.3629 (2)	0.0443 (6)	0.0323 (2)
C(4)	0.3347 (7)	0.6612 (3)	0.2782 (13)	0.2896 (2)	0.0316 (6)	0.0794 (2)
C(5)	0.3841 (7)	0.6308 (3)	0.0933 (12)	0.2728 (2)	0.2015 (6)	0.1494 (2)
C(6)	0.5240 (6)	0.6293 (3)	0.0546 (10)	0.3303 (2)	0.3776 (5)	0.1718 (2)
C(7)	0.6337 (7)	0.5458 (3)	—0.0970 (11)	0.3589 (2)	0.5567 (6)	0.3208 (2)
C(8)	0.8143 (7)	0.6909 (3)	—0.0154 (10)	0.5355 (2)	0.5581 (5)	0.1726 (2)
C(9)	0.6788 (8)	0.5190 (3)	—0.3214 (11)	0.3449 (2)	0.7856 (6)	0.3753 (2)
C(10)	0.9660 (7)	0.6793 (3)	—0.0341 (13)	0.5718 (2)	0.7873 (6)	0.2122 (2)
C(11)	0.8319 (9)	0.5018 (4)	—0.3019 (14)	0.3721 (2)	0.7641 (6)	0.4796 (2)
C(12)	1.0075 (7)	0.6585 (3)	—0.2725 (14)	0.5884 (2)	0.7657 (6)	0.3190 (2)
C(13)	0.9273 (7)	0.5518 (3)	—0.2159 (12)	0.3743 (2)	1.0093 (6)	0.5290 (2)
C(14)	0.9172 (9)	0.6055 (3)	—0.3679 (12)	0.6055 (2)	1.0113 (6)	0.3651 (2)
O(1)	0.5726 (5)	0.5995 (2)	—0.1393 (7)	0.3118 (1)	0.5567 (4)	0.2383 (1)
O(2)	0.6428 (5)	0.5249 (2)	0.0894 (8)	0.4061 (2)	0.3967 (4)	0.3413 (1)
O(3)	0.7596 (4)	0.6577 (2)	0.1561 (7)	0.4538 (1)	0.5893 (3)	0.1488 (1)
O(4)	0.7450 (5)	0.7241 (2)	—0.1278 (8)	0.5702 (1)	0.3677 (4)	0.1634 (2)

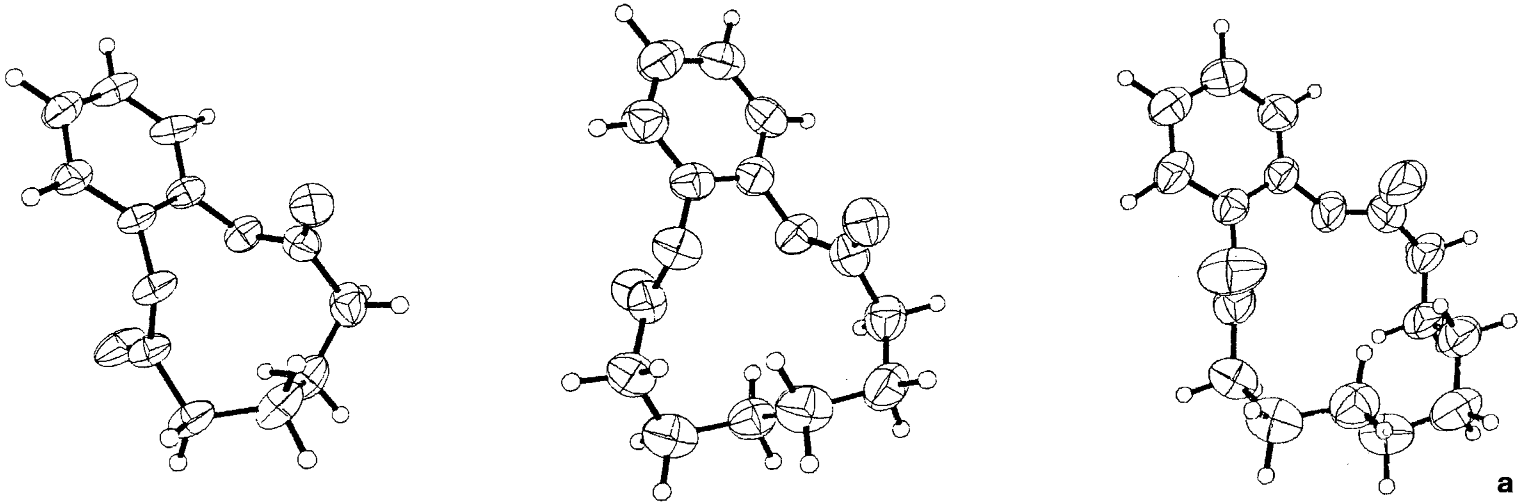
Table 6. *Final atomic coordinates of non hydrogen atoms with estimated standard deviations in parentheses for cyclich esters of pyrocatechol and sebacic acid ($x = 8$)*

	cyclic monomer **2**			cyclic dimer **3**		
	x	y	z	x	y	z
C(1)	0.5298 (5)	—0.2828 (7)	0.3568 (8)	0.1467 (1)	0.6486 (6)	0.3263 (2)
C(2)	0.4649 (6)	—0.4526 (8)	0.2679 (9)	0.0933 (2)	0.8297 (6)	0.3064 (2)
C(3)	0.3763 (5)	—0.5209 (8)	0.0937 (9)	0.0482 (2)	0.8161 (7)	0.3515 (3)
C(4)	0.3504 (5)	—0.4148 (8)	0.0130 (9)	0.0569 (2)	0.6243 (7)	0.4151 (3)
C(5)	0.4167 (5)	—0.2433 (8)	0.1018 (8)	0.1110 (2)	0.4430 (7)	0.4351 (2)
C(6)	0.5075 (4)	—0.1775 (7)	0.2713 (7)	0.1556 (2)	0.4588 (6)	0.3893 (2)
C(7)	0.6427 (5)	0.0634 (8)	0.2874 (9)	0.2779 (1)	0.2902 (5)	0.4804 (2)
C(8)	0.7182 (5)	—0.2215 (8)	0.5783 (9)	0.1757 (2)	0.5533 (7)	0.1979 (2)
C(9)	0.6955 (6)	0.2528 (7)	0.4030 (10)	0.3224 (2)	0.0630 (5)	0.4886 (2)
C(10)	0.7904 (6)	—0.1254 (9)	0.7845 (9)	0.2254 (2)	0.6342 (8)	0.1551 (2)
C(11)	0.8210 (6)	0.3205 (8)	0.3948 (10)	0.4070 (2)	0.0908 (6)	0.5598 (2)
C(12)	0.8577 (6)	0.0601 (8)	0.8375 (9)	0.3097 (2)	0.6370 (6)	0.2284 (2)
C(13)	0.9140 (6)	0.2626 (8)	0.4920 (10)	0.4475 (2)	—0.1568 (6)	0.5795 (2)
C(14)	0.9600 (6)	0.0807 (9)	0.7586 (10)	0.3435 (2)	0.3810 (6)	0.2631 (2)
C(15)	0.9495 (7)	0.3465 (8)	0.7102 (11)	0.4674 (2)	0.1378 (6)	0.3521 (2)
C(16)	1.0241 (6)	0.2654 (9)	0.8038 (10)	0.4289 (2)	0.3889 (6)	0.3299 (2)
O(1)	0.5731 (3)	—0.0049 (4)	0.3693 (5)	0.2074 (1)	0.2700 (4)	0.4032 (2)
O(2)	0.6554 (5)	—0.0189 (6)	0.1428 (7)	0.2977 (1)	0.4656 (4)	0.5335 (2)
O(3)	0.6097 (4)	—0.2055 (6)	0.5429 (6)	0.1949 (1)	0.6731 (4)	0.2850 (2)
O(4)	0.7499 (4)	—0.3023 (9)	0.4550 (8)	0.1251 (1)	0.4127 (6)	0.1621 (2)

Table 7. *Selected bond lengths (Å), bond angles (°) and torsion angles (°)*

	cyclic monomers **2**			cyclic dimers **3**		
	$x = 4$ $n = 12$	$x = 6$ $n = 14$	$x = 8$ $n = 16$	$x = 4$ $n = 12$	$x = 6$ $n = 14$	$x = 8$ $n = 16$
C(6)—O(1)	1.399 (4)	1.404 (8)	1.388 (7)	1.394 (4)	1.401 (4)	1.404 (4)
C(1)—O(3)	1.395 (4)	1.401 (8)	1.401 (8)	1.392 (4)	1.400 (3)	1.400 (4)
O(1)—C(7)	1.369 (4)	1.378 (8)	1.353 (8)	1.376 (4)	1.369 (4)	1.352 (4)
O(3)—C(8)	1.379 (4)	1.365 (8)	1.328 (9)	1.366 (4)	1.365 (4)	1.365 (4)
C(7)—O(2)	1.194 (5)	1.183 (8)	1.182 (9)	1.183 (4)	1.195 (4)	1.189 (4)
C(8)—O(4)	1.194 (5)	1.192 (8)	1.181 (11)	1.182 (4)	1.199 (4)	1.178 (5)
C(7)—C(9)	1.493 (5)	1.511 (10)	1.497 (11)	1.494 (5)	1.499 (5)	1.494 (5)
C(8)—C(10)	1.489 (6)	1.488 (10)	1.495 (11)	1.501 (5)	1.492 (4)	1.504 (6)
C(1)—C(6)—O(1)	117.9 (3)	119.7 (5)	118.1 (6)	119.9 (3)	119.6 (3)	119.5 (3)
C(6)—C(1)—O(3)	118.6 (3)	120.2 (6)	117.8 (6)	120.5 (3)	115.3 (2)	120.6 (3)
C(5)—C(6)—O(1)	121.1 (3)	119.2 (6)	121.9 (6)	119.9 (3)	119.4 (3)	119.7 (3)
C(2)—C(1)—O(3)	120.7 (3)	119.9 (6)	121.8 (6)	118.7 (3)	124.0 (3)	118.2 (3)
C(1)—O(3)—C(8)	116.9 (3)	117.8 (5)	120.7 (6)	119.4 (3)	121.0 (2)	117.8 (3)
C(6)—O(1)—C(7)	118.0 (3)	115.8 (5)	117.9 (5)	118.0 (3)	116.4 (2)	118.0 (3)
O(1)—C(7)—O(2)	122.2 (3)	122.8 (6)	123.0 (6)	122.3 (3)	122.5 (3)	122.2 (3)
O(3)—C(8)—O(4)	122.0 (3)	122.2 (6)	121.3 (8)	121.8 (3)	122.6 (3)	122.7 (4)
O(1)—C(7)—C(9)	110.6 (3)	109.5 (5)	110.1 (6)	109.5 (3)	110.3 (3)	110.2 (3)
O(3)—C(8)—C(10)	110.6 (3)	110.3 (5)	112.2 (6)	110.2 (3)	110.6 (3)	110.7 (3)
O(2)—C(7)—C(9)	127.1 (3)	127.6 (6)	126.9 (7)	128.1 (3)	127.1 (3)	127.6 (3)
O(4)—C(8)—C(10)	127.3 (4)	127.5 (6)	126.5 (8)	127.9 (3)	126.8 (3)	126.5 (4)
C(5)—C(6)—O(1)—C(7)	111.4	—104.5	—65.3	—79.4	115.0	—89.6
C(2)—C(1)—O(3)—C(8)	112.3	—106.0	79.1	—102.8	—54.9	—95.6
C(6)—O(1)—C(7)—O(2)	—13.5	1.6	—4.7	—8.2	—9.1	—3.0
C(1)—O(3)—C(8)—O(4)	—13.4	2.7	—0.8	—1.9	9.1	—7.8

C(6)—O(1)—C(7)—C(9)	164.0	179.4	173.8	169.0	168.0	174.9
C(1)—O(3)—C(8)—C(10)	164.1	—177.5	178.3	175.6	—169.6	170.0
O(1)—C(7)—C(9)—C(11)	—63.7	127.1	146.4	165.1	161.3	168.1
O(3)—C(8)—C(10)—C(12)	—65.9	122.7	—86.7	53.2	107.4	47.8
O(2)—C(7)—C(9)—C(11)	113.7	—55.2	—35.2	—17.9	—21.7	—14.1
O(4)—C(8)—C(10)—C(12)	111.4	—57.6	92.3	—129.6	—71.2	—134.5
C(*n*-9)—C(*n*-7)—C(*n*-5)—C(*n*-3)	—	—	—67.4	—	—	169.9
C(*n*-7)—C(*n*-5)—C(*n*-3)—C(*n*-1)	—	—51.9	—71.1	—	168.1	178.3
C(*n*-5)—C(*n*-3)—C(*n*-1)—C(*n*)	—54.4	—57.7	169.4	165.7	175.3	177.4
C(*n*-3)—C(*n*-1)—C(*n*)—C(*n*-2)	122.4	176.4	—65.1	—178.6	169.9	—179.1
C(*n*-1)—C(*n*)—C(*n*-2)—C(*n*-4)	—55.9	—60.1	—66.8	—75.7	177.6	—169.8
C(*n*)—C(*n*-2)—C(*n*-4)—C(*n*-6)	—	—50.9	177.4	—	—166.1	175.5
C(*n*-2)—C(*n*-4)—C(*n*-6)—C(*n*-8)	—	—	—70.3	—	—	68.1


a

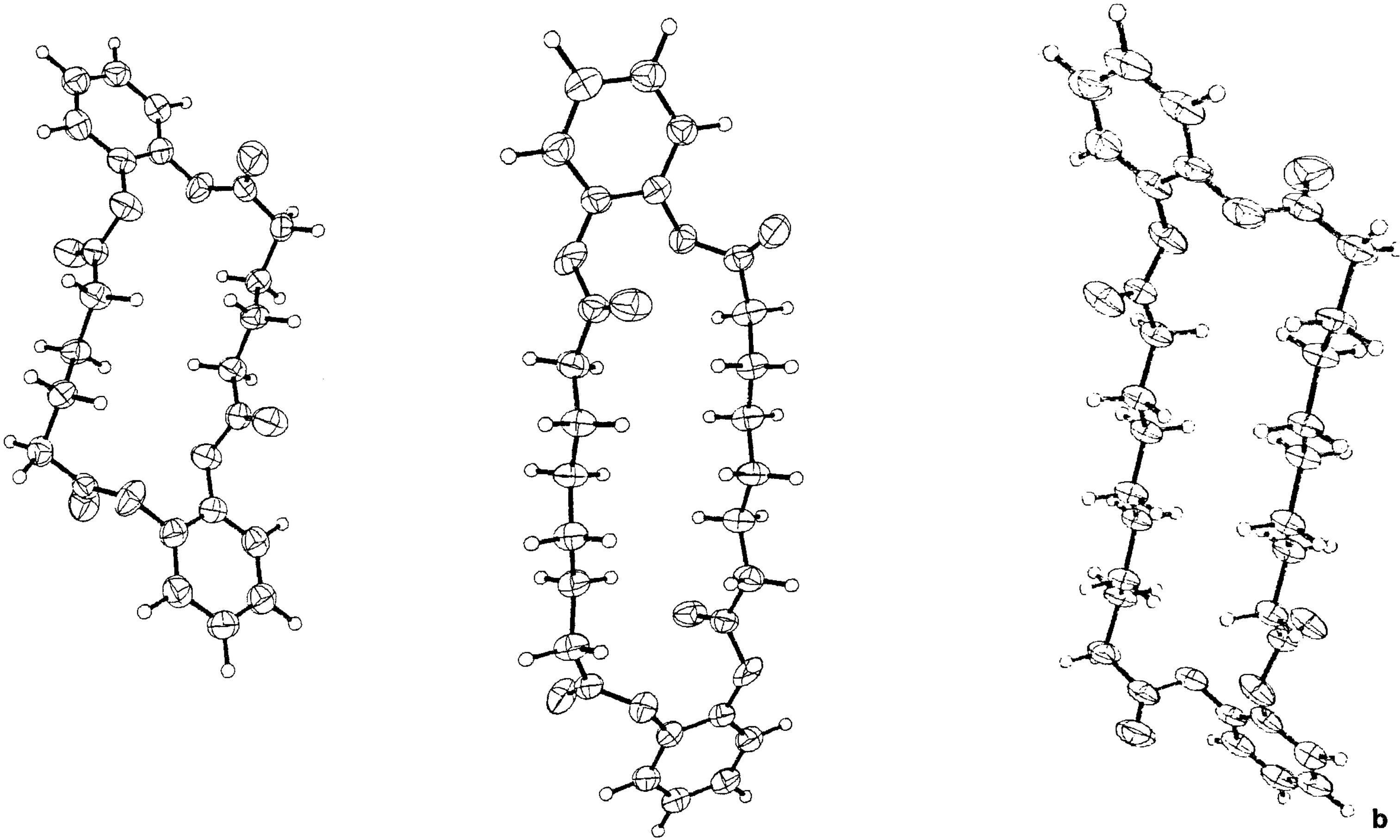
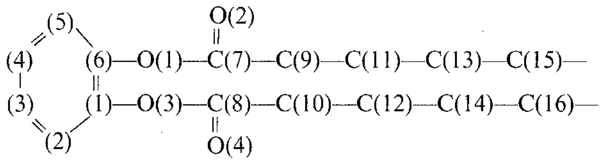


Fig. 1. Molecular conformation of cyclic esters **2** (*a*) and **3** (*b*) with $x = 4$, $x = 6$ and $x = 8$ (from the left to the right)

(of course the esters with $x = 4$ and $x = 6$ contain only 12 and 14 C-atoms):



Each of the cyclic dimers is situated on a crystallographic center of symmetry. Thus, these molecules are centrosymmetric. The bond lengths and bond angles in the aromatic residue and in the aliphatic chain are close to the expected values. The bond lengths and angles around the ester function also do not show any significant differences which could be attributed to the monomeric or dimeric structure or to the chain length of the diacid.

Conformational differences are reflected by torsion angles (compare Fig. 1). In all dimers one of the O—CO—$(CH_2)_n$-chains extends straight from the aromatic ring, while the other O—CO—$(CH_2)_n$-chain bends around the CH_2-unit adjacent to the O—CO-group. The two aliphatic chains in each dimer are roughly parallel.

The ester group (—O—CO—C—) forms a plane which also nearly contains the adjacent aromatic carbon C(1) or C(6) (*s*-trans conformation, see above). The strongest deviation of about 15° by rotation around the O—CO-bond is observed for **2** ($x = 4$). These planes and the aromatic plane include an angle which varies between 55° [C(8)—O(3)—C(1)—C(2) in **3** ($x = 6$)] and 90° [C(5)—C(6)—O(1)—C(7) in **3** ($x = 8$)]. Both carbonyl groups are at the same side of the aromatic ring in **2** ($x = 8$), while they are situated at opposite sides in **2** ($x = 4$ and $x = 6$). As evident from the torsion angles, the latter compounds have approximate two-fold symmetry. On the other hand in the cyclic dimers **3** the carbonyl groups are close to parallel for $x = 6$, and antiparallel for $x = 4$ and $x = 8$.

The aliphatic chain between the carbonyl groups has a complete *trans*-zigzag arrangement (*anti*-conformation) for **3** ($x = 6$), while one *gauche*-conformation is found in **3** for $x = 4$ and $x = 8$. The observed torsion angles do not differ more than 15° from 180° or 60°. In the cyclic monomers *gauche* conformations occur more frequently (for $x = 6$ only one *anti*- and for $x = 8$ two *anti*-conformations are observed) and for $x = 4$ one torsion angle comes near to 120°.

However, on the basis of the present results it is not possible to decide, wether the differences are caused by packing effects rather than by the different ring size.

Experimental Part

Preparation of Hydroquinone Esters **1**

A solution of 3.3 g (0.03 mol) hydroquinone and 30 cm^3 pyridine in 200 cm^3 benzene and a solution of 0.03 mol diacid chloride in 200 cm^3 benzene were added simultaneously during 5 to 8 h to 1 dm^3 of boiling benzene. Refluxing was continued for 1 h and 1 dm^3 benzene was removed by distillation. The crystalline precipitate (A) containing most of the pyridine hydrochloride was separated from the warm solution. After cooling a small quantity of a second precipitate (B) was obtained, and finally the filtrate was evaporated *in vacuo* to give a solid residue (C). Further details:

Adipic acid ($x = 4$): (A) was dissolved in dimethylsulfoxide, reprecipitated in water and recrystallized from acetone, (B) was directly recrystallized from chloroform, and (C) was suspended in acetone, poured in water and the precipitate recrystallized from chloroform. An identical product (**1**) was obtained from all fractions.

Suberic acid ($x = 6$): (A) was dissolved in acetone, reprecipitated in water and recrystallized from chloroform. (B) was directly pure and (C) was purified by column chromatography (silica gel, chloroform), where the first fractions contained the cyclic dimer **1**.

Sebacic acid ($x = 8$): (A) was reprecipitated from acetone/water and recrystallized from chloroform. (B) and (C) were purified by column chromatography (silica gel, chloroform or methylene chloride) and further recrystallization from methylene chloride/petroleum ether (40–80°). The identical cyclic dimer **1** was obtained in all cases.

Preparation of Pyrocatechol Esters **2** *and* **3**

A solution of 3.3 g (0.03 mol) pyrocatechol and 6.06 g (0.06 mol) triethylamine in 200 cm^3 benzene and a solution of 0.03 mol diacid chloride in 200 cm^3 benzene were added simultaneously during 5 to 8 h to 1 dm^3 of boiling, dry benzene. After addition of further 0.6 g triethylamine refluxing was continued for 1 h and finally fractions (A), (B), and (C) were isolated as described above. In all cases (A) consisted only of triethylamine hydrochloride. Further details:

Succinic acid ($x = 2$): (B) was recrystallized twice from methylene chloride, (C) was purified by column chromatography (silica gel, chloroform). The first fractions gave the identical dimeric product **3**.

Adipic acid ($x = 4$): (B) was not obtained. (C) was separated by column chromatography (silica gel, chloroform). From the first fractions pure cyclic monomer **2** was obtained after recrystallization from chloroform/petroleum ether (40–70°). Further fractions contained the cyclic dimer **3** which was recrystallized from chloroform.

Suberic acid ($x = 6$): (B) was not obtained. (C) was separated by column chromatography (silica gel, methylene chloride) to yield in the first fractions cyclic monomer **2**, later cyclic dimer **3**, which were both recrystallized from chloroform/petroleum ether (40–70°).

Sebacic acid ($x = 8$): (B) was nearly pure cyclic dimer **3** which was further recrystallized from acetone. (C) was dissolved in petroleum ether (40–70°)/chloroform 1 : 2, where a small amount of the dimer **3** remained insoluble, and purified by column chromatography (silica gel). The first fractions contained the cyclic monomer **2** which was recrystallized from petroleum ether (40–70°).

All compounds gave satisfactory values in C,H-elemental analysis. Further data are collected in Tables 1 and 2. Single crystals for X-ray analysis were obtained by recrystallization from chloroform (**2** and **3** with $x = 4$), from cyclohexane (**2**, $x = 8$) and from acetone (**3**, $x = 8$), or by keeping a solution in dimethyl sulfoxide over a longer period at the open air (**2** and **3** with $x = 6$).

Crystallographic Measurements

The diffraction data for each crystal were measured at room temperature on a microcomputer-controlled four-circle diffractometer[13]. The unit cell constants were derived from a least-squares fit to the observed values of $\pm\theta$ for at least 13 reflections. The crystal data are given in Table 3. The intensities were measured up to $2\theta = 120°$ by a θ—2θ scan technique using Ni-filtered Cu Kα radiation. The reflections whose intensities were greater than $2\sigma(I)$ were used for subsequent calculations. Periodically monitored reflections showed no significant change in intensity. The intensities were corrected for the *Lorentz* and polarization factors.

Structure Determination

The structure was solved by the direct method[14], and refined by the block-diagonal least-squares method[15]. The hydrogen atoms were located in the difference *Fourier* synthesis calculated after the anisotropic refinement for nonhydrogen atoms and included in the subsequent refinement. The extinction correction was made for several strongest reflections. The weighting scheme used in the final cycle of the refinement and the final R values are also given in Table 3. The atomic scattering factors were taken from the International Tables for X-ray Crystallography[16]. All the calculations were performed on a HITAC M-150 computer at the Tottori University Computing Center.

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