Acta Cryst. (1976). B32, 847

The Structures of the Octaacetate Esters of Two Condensation Tetramers of Resorcinol with *p*-Bromobenzaldehyde, $C_{68}H_{52}O_{16}Br_4$

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(*Received* 28 *July* 1975; *accepted* 30 *July* 1975)

Two isomers were separated from the condensation reaction between resorcinol and *p*-bromobenzaldehyde. Both isomers contain four resorcinol units and four *p*-bromobenzylidene units. The structures of the octaacetate esters of both isomers, referred to as (I) and (II), have been determined. (I) has a twofold axis of symmetry and the benzene rings have the same configuration as found for the octabutyrate ester by Nilsson [*Acta Chem. Scand.* (1968). **22**, 732–747]. (II) has a center of symmetry with pairs of *p*-bromophenyl groups on opposite sides of the molecule. The crystal data are: (I), $a=24\cdot229$ (8), $b=11\cdot959$ (5), $c=24\cdot334$ (8) Å, $\beta=110\cdot24$ (1)°, space group $C2/c$, $Z=4$; (II), $a=16\cdot894$ (5), $b=14\cdot051$ (5), $c=13\cdot348$ (4) Å, $\beta=92\cdot38$ (1)°, space group $P2_1/n$, $Z=2$. The final R_1 index for (I) is 0·117 without H atoms and for (II), 0·043 with H atoms.

Introduction

Although few *o*-quinone methides have been described it has often been considered that they are the reactive intermediates in many phenol condensation reactions. In an attempt to synthesize *o*-quinone methides a variety of aromatic aldehydes were condensed with methoxyquinol and resorcinol in aqueous organic acid solutions. Methoxyquinol unexpectedly yielded colorless 9-phenylxanthylium salts (Jurd, 1975). Resorcinol, on the other hand, condensed with anisaldehyde, veratraldehyde, and *p*-bromobenzaldehyde to give a series of high melting point, highly insoluble compounds, one of which is identical with a cyclooligomeric phenol previously obtained by Erdtman & Högberg (1968) by condensation in the presence of hydrogen chloride.

Erdtman & Högberg (1968) pointed out that these cyclooligomers have four possible geometrical configurations. From the reaction of resorcinol with *p*-bromobenzaldehyde they isolated one isomer and Nilsson (1968) established, by the structure determination of the octabutyrate ester, that this isomer had configuration (I), Fig. 1. Crystals of the octabutyrate ester are triclinic and the molecules have no symmetry.

In our work two crystalline products were obtained and their octaacetate esters prepared. These two esters will be referred to as (I) and (II). The crystal structures of (I) and (II) have been determined and the results are reported in this paper.

Experimental

A solution of resorcinol (4·40 g) and 4-bromobenzaldehyde (7·40 g; 1 mol eq.) in formic acid (20·0 ml) and water (10·0 ml) was boiled under reflux for 5 h. The cream-colored crystalline product (10·8 g), $(C_{13}HgBrO_2)_n$, was collected and fractionally recrystallized from acetone–methanol to give minor product (0·90 g), m.p. > 325° and major product (7·1 g), m.p. > 325°. When the minor product was warmed with acetic anhydride and pyridine, an octaacetate, (I), was formed, which crystallized from acetone–methanol as colorless needles, m.p. > 360°. (Found: C, 56·4; H, 3·69. Calculated for $C_{68}H_{52}O_{16}Br_4$: C, 56·6; H, 3·60.) The major product gave a different acetate (II) which crystallized from chloroform–acetone as colorless needles, m.p. > 360°, which was depressed to 340–355° by admixture with the octaacetate (I). (Found: C, 56·5; H, 3·64;

Table 1. *Crystal data for the octaacetate esters of two condensation tetramers*

	(I)	(II)
Formula	$C_{68}H_{52}O_{16}Br_4$	$C_{68}H_{52}O_{16}Br_4$
Systematic absences	hkl: $h+k\neq 2n$ $h0l$: $h+l\neq 2n$	$h0l$: $h+l\neq 2n$ $0k0$: $k\neq 2n$
Space group	$C2/c$	$P2_1/n$
a	24·229 (8) Å	16·894 (5) Å
b	11·959 (5)	14·051 (5)
c	24·334 (8)	13·348 (4)
β	110·24 (1)°	92·38 (1)°
F. W.	1443·6	1443·6
Z	4	2
$F(000)$	2912	1456
D_c	1·450 g cm^{-3}	1·515 g cm^{-2}
D_m	1·47 g cm^{-3}	1·50 g cm^{-3}
Number of parameters refined	397	501
μ(Cu $K\alpha$)	38·36 cm^{-1}	40·08 cm^{-1}
λ(Cu $K\alpha_1$)	1·5405 Å	
λ(Cu $K\alpha_2$)	1·5443	
λ(Cu $K\alpha$)	1·5418	

GE-XRD6 automatic diffractometer. $\theta/2\theta$ scan technique, 1° min^{-1}, scan range varied to include both α_1 and α_2 peaks.

CH_3CO–, 24·3. Calculated for $C_{68}H_{52}O_{16}Br_4$: C, 56·6; H, 3·60; $4CH_3CO$–, 23·8.)

The n.m.r. spectrum of (I) showed: δ2·00 $(3H,S)_{n/2}$ acetate, δ2·06 $(3H,S)_{n/2}$ acetate, δ5·36 $(2H,S)_{n/2}$ methine, δ5·78 $(1H,S)_{n/2}$ resorcinol proton adjacent to oxygen, δ6·04 $(1H,S)_{n/2}$ resorcinol proton adjacent to oxy-

Table 2. *Positional* (× 10^4) *and thermal parameters and their estimated standard deviations, in parentheses, for* (I), $C_{68}H_{52}O_{16}Br_4$

The thermal parameters are in Å^2. The temperature factor is exp (− T) where $T=\frac{1}{4}\sum h_ih_jB_{ij}a_i^*a_j^*$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	1942 (1)	−3507 (2)	3568 (2)	15·5 (2)	5·5 (1)	21·8 (3)	4·1 (1)	11·8 (2)	1·8 (1)
Br(2)	−2176 (1)	−2946 (2)	3023 (1)	12·9 (2)	9·8 (2)	10·1 (2)	7·1 (1)	1·9 (1)	0·6 (1)
O(1)	1454 (5)	1011 (9)	4930 (5)	4·6 (6)	5·7 (6)	4·0 (5)	0·6 (5)	0·9 (5)	0·3 (5)
O(2)	1676 (6)	2750 (9)	5257 (6)	8·4 (8)	7·0 (8)	9·6 (9)	−0·1 (7)	−2·3 (7)	−2·3 (7)
O(3)	−0590 (4)	1298 (8)	4653 (4)	6·0 (6)	5·3 (6)	4·5 (5)	0·3 (4)	2·6 (5)	0·7 (5)
O(4)	−0422 (9)	2910 (9)	5080 (9)	21·9 (2)	9·9 (1)	30·9 (3)	−4·1 (1)	21·6 (2)	−10·6 (2)
O(5)	−0782 (5)	3971 (9)	3359 (5)	6·5 (7)	5·5 (6)	5·1 (7)	−1·1 (5)	3·0 (6)	−0·1 (5)
O(6)	−1673 (8)	4120 (9)	3310 (8)	10·9 (1)	13·8 (1)	15·2 (2)	−2·4 (1)	7·0 (1)	4·2 (1)
O(7)	−1157 (4)	3740 (7)	1292 (4)	6·3 (6)	3·8 (5)	3·3 (6)	0·4 (4)	1·0 (4)	−0·2 (4)
O(8)	−0404 (6)	4930 (9)	1630 (5)	8·2 (9)	13·9 (1)	8·2 (9)	5·4 (8)	3·1 (7)	−0·0 (8)
C(1)	1740 (9)	−1950 (9)	3587 (9)	9·9 (1)	5·0 (1)	9·4 (1)	3·7 (1)	6·6 (1)	2·5 (9)
C(2)	1159 (9)	−1690 (9)	3403 (8)	7·5 (1)	4·9 (1)	7·6 (1)	1·6 (8)	2·5 (1)	0·7 (8)
C(3)	0996 (7)	−0580 (9)	3437 (7)	6·3 (1)	3·3 (8)	7·7 (1)	−0·9 (7)	3·5 (8)	−1·6 (7)
C(4)	1422 (7)	0230 (9)	3670 (6)	4·4 (9)	4·9 (1)	5·4 (9)	1·8 (8)	2·5 (8)	1·3 (7)
C(5)	2013 (8)	−0080 (9)	3860 (8)	7·5 (1)	4·4 (9)	12·0 (1)	1·0 (8)	5·3 (1)	2·0 (9)
C(6)	2184 (9)	−1190 (9)	3800 (9)	8·3 (1)	6·1 (1)	11·8 (2)	−0·3 (1)	4·8 (1)	1·6 (1)
C(7)	1275 (6)	1450 (9)	3739 (6)	4·0 (8)	3·4 (7)	4·0 (8)	1·0 (6)	1·8 (6)	1·0 (6)
C(8)	0776 (6)	1470 (9)	3985 (6)	3·2 (8)	3·7 (7)	3·3 (8)	−0·5 (6)	0·9 (7)	−0·3 (6)
C(9)	0893 (7)	1310 (9)	4576 (6)	3·2 (9)	4·1 (7)	2·8 (8)	0·3 (6)	−0·1 (8)	−0·1 (6)
C(10)	0466 (8)	1280 (9)	4831 (7)	3·9 (9)	3·9 (7)	4·8 (8)	0·2 (6)	1·0 (9)	0·4 (6)
C(11)	−0109 (8)	1420 (9)	4448 (7)	6·2 (1)	3·6 (7)	3·7 (9)	−0·3 (7)	3·2 (9)	−0·6 (7)
C(12)	−0264 (6)	1570 (9)	3855 (6)	4·0 (8)	3·4 (7)	3·7 (8)	0·0 (6)	1·1 (7)	−0·5 (6)
C(13)	0189 (7)	1630 (9)	3616 (6)	3·4 (8)	3·0 (7)	4·4 (8)	0·1 (5)	1·6 (8)	−0·2 (6)
C(14)	−0923 (6)	1640 (9)	3454 (6)	3·7 (8)	4·9 (8)	2·9 (7)	0·1 (6)	1·4 (6)	−0·4 (6)
C(15)	−1197 (7)	0440 (9)	3364 (6)	5·1 (1)	5·3 (9)	2·8 (7)	1·3 (8)	1·9 (7)	−0·1 (6)
C(16)	−1814 (8)	0430 (9)	3161 (7)	3·3 (9)	8·7 (1)	6·5 (1)	0·2 (8)	1·1 (8)	−1·7 (8)
C(17)	−2110 (9)	−0610 (9)	3052 (8)	8·2 (1)	8·8 (1)	6·9 (1)	4·0 (1)	1·1 (1)	−3·4 (2)
C(18)	−1770 (9)	−1590 (9)	3149 (8)	6·1 (1)	6·6 (1)	6·9 (1)	3·5 (1)	0·4 (9)	−1·1 (9)
C(19)	−1189 (9)	−1550 (9)	3342 (8)	7·4 (1)	4·7 (1)	8·1 (1)	0·6 (9)	2·5 (1)	−0·3 (8)
C(20)	−0869 (7)	−0510 (9)	3467 (7)	6·7 (1)	2·9 (8)	8·3 (1)	0·3 (8)	3·6 (8)	−0·4 (7)
C(21)	−0998 (5)	2180 (9)	2367 (6)	3·1 (7)	3·8 (8)	4·3 (9)	−0·7 (6)	1·4 (6)	−0·5 (7)
C(22)	−0934 (5)	3370 (9)	2836 (7)	3·3 (7)	4·3 (9)	2·9 (9)	−0·3 (6)	0·7 (6)	1·2 (7)
C(23)	−0993 (6)	3900 (9)	2329 (7)	4·7 (8)	4·5 (8)	2·8 (8)	−0·8 (6)	1·4 (6)	−0·5 (7)
C(24)	−1088 (6)	3260 (9)	1831 (6)	4·6 (8)	4·1 (8)	2·0 (8)	−0·7 (6)	0·9 (6)	−0·9 (7)
C(25)	−1143 (5)	2080 (9)	1827 (6)	1·8 (6)	4·5 (9)	4·2 (9)	−0·2 (5)	0·8 (6)	0·4 (7)
C(26)	−1098 (6)	1580 (9)	2354 (7)	3·3 (7)	5·2 (8)	3·0 (8)	−0·9 (6)	1·4 (6)	−0·3 (8)
C(27)	1820 (9)	1790 (9)	5263 (8)	10·7 (2)	5·2 (1)	5·4 (1)	−1·4 (1)	3·2 (1)	−0·8 (1)
C(28)	2419 (7)	1260 (9)	5625 (8)	3·1 (8)	9·6 (1)	8·3 (1)	0·8 (8)	−1·8 (8)	2·7 (1)
C(29)	−0730 (9)	2100 (9)	4950 (9)	15·2 (2)	4·0 (1)	12·1 (2)	−0·1 (1)	8·3 (2)	−2·4 (1)
C(30)	−1302 (9)	1890 (9)	5057 (9)	9·1 (1)	8·8 (1)	12·7 (2)	0·5 (1)	9·2 (1)	0·6 (1)
C(31)	−1130 (9)	4450 (9)	3550 (9)	6·1 (2)	11·5 (2)	11·8 (2)	−1·7 (1)	0·6 (2)	−1·0 (2)
C(32)	−0910 (9)	5110 (9)	4098 (8)	13·2 (2)	11·7 (2)	5·9 (1)	0·2 (1)	2·5 (1)	6·2 (1)
C(33)	−0774 (9)	4540 (9)	1213 (9)	7·5 (1)	5·4 (1)	6·9 (1)	1·9 (9)	3·7 (1)	0·1 (9)
C(34)	−0893 (9)	4770 (9)	0600 (8)	14·3 (2)	11·1 (1)	3·5 (9)	5·8 (1)	2·1 (1)	−2·1 (9)

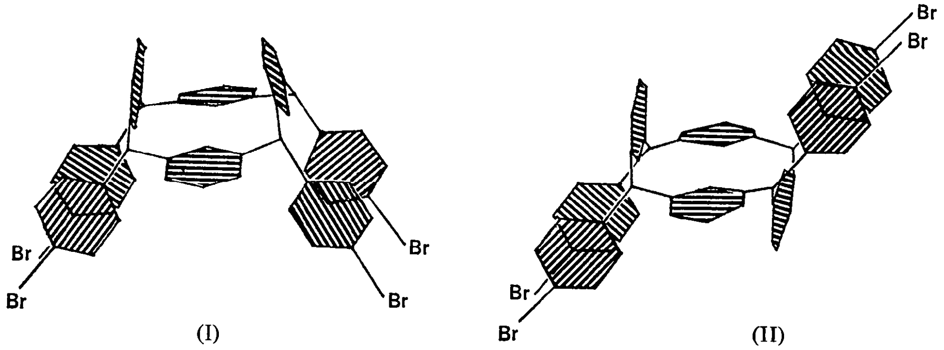

Fig. 1. The molecular configuration of the benzene rings in (I) and (II).

gen, $\delta 6{\cdot}54$ $(4\text{H}, d, J=8\text{Hz})_{n/2}$ aromatic protons, $\delta 6{\cdot}89$ $(1\text{H}, S)_{n/2}$ resorcinol proton, $\delta 7{\cdot}13$ $(1\text{H}, S)_{n/2}$ resorcinol proton, $\delta 7{\cdot}78$ $(4\text{H}, d, J=8\text{Hz})_{n/2}$ aromatic protons adjacent to bromine. The n.m.r. spectrum of (II) showed: $\delta 2{\cdot}01$ $(3\text{H}, S)_{n/2}$ acetate, $\delta 2{\cdot}06$ $(3\text{H}, S)_{n/2}$ acetate, $\delta 5{\cdot}45$ $(2\text{H}, S)_{n/2}$ methine, $\delta 5{\cdot}90$ $(1\text{H}, S)_{n/2}$ resorcinol proton adjacent to oxygen, $\delta 6{\cdot}20$ $(1\text{H}, S)_{n/2}$ resorcinol proton adjacent to oxygen, $\delta 6{\cdot}56$ $(4\text{H}, d, J=8\text{Hz})_{n/2}$ aromatic proton, $\delta 6{\cdot}89$ $(1\text{H}, S)_{n/2}$ resorcinol proton, $\delta 7{\cdot}06$ $(1\text{H}, S)_{n/2}$ resorcinol proton, $\delta 7{\cdot}24$ $(4\text{H}, d, J=8\text{Hz})_{n/2}$ aromatic proton adjacent to bromine.

Crystals of both (I) and (II) suitable for X-ray analysis were obtained from CHCl_3. Weissenberg and precession photographs were used to establish the space group for each isomer. The systematic absences and the space group are given in Table 1. Lattice constants were obtained by averaging the results obtained from high angle $\theta/2\theta$ scans. The crystal data for (I) and (II) are summarized in Table 1.

The crystals selected for intensity measurements had a maximum size of 0·3 mm. The intensity data were not corrected for absorption or secondary extinction. Ni-filtered copper radiation was detected by a scintillation counter coupled with a single-channel pulse-height analyzer. Backgrounds were measured at 0·5° on each side of the scan limits. 3527 reflections were measured for (I); 3383 of these were unique, 330 measured as zero and 463 other reflections had $I<2\sigma(I)$. 3931 reflections were measured for (II), 3288 of which were unique, 170 were measured as zero, and 288 other reflections had $I \leq \sigma(I)$. $\sigma(I)$ was calculated from the expression $\sigma(I)=[C+(T_c/2T_b)^2(B_1+B_2)]^{1/2}$ where C is total counts in scan time T_c, B_1 and B_2 are the two background counts taken for $T_b=20$ s. To reduce the

Table 3. *Positional* ($\times 10^4$ *for heavy atoms,* $\times 10^3$ *for* H) *and thermal parameters and their estimated standard deviations, in parentheses, for* (II), $\text{C}_{68}\text{H}_{52}\text{O}_{16}\text{Br}_4$

The thermal parameters are in Å². The temperature factor is $\exp(-T)$ where $T=\frac{1}{4}\sum h_i h_j B_{ij} a_i^* a_j^*$ for the anisotropic case and $T=B(\sin\theta/\lambda)^2$ for the isotropic case.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	1442 (2)	3446 (5)	−3805 (4)	8·6 (5)	7·8 (5)	4·5 (3)	1·4 (2)	0·8 (3)	2·1 (2)
Br(2)	−1580 (3)	−1041 (3)	5505 (4)	7·3 (4)	6·7 (4)	4·7 (3)	−0·2 (2)	0·8 (3)	2·4 (2)
O(1)	2555 (2)	2304 (3)	1779 (2)	3·1 (2)	4·5 (2)	5·0 (2)	−1·2 (1)	−0·5 (1)	−0·4 (1)
O(2)	2337 (3)	3708 (3)	1051 (4)	6·7 (3)	6·9 (3)	9·5 (3)	−1·6 (2)	1·3 (2)	2·6 (2)
O(3)	0121 (2)	2662 (2)	3396 (2)	4·2 (2)	3·9 (2)	3·2 (2)	−0·2 (1)	0·1 (1)	−0·6 (1)
O(4)	−0251 (3)	3970 (3)	2552 (3)	10·0 (3)	5·7 (2)	6·0 (2)	2·9 (2)	−0·7 (2)	−0·1 (2)
O(5)	−1426 (2)	2784 (2)	0503 (2)	5·1 (2)	3·3 (2)	3·4 (1)	−0·5 (1)	−0·2 (1)	0·4 (1)
O(6)	−0729 (3)	3093 (3)	−0840 (4)	8·5 (3)	6·0 (3)	9·3 (3)	0·2 (2)	3·8 (3)	2·1 (2)
O(7)	−2390 (2)	0215 (2)	−1580 (2)	4·0 (2)	5·6 (2)	2·7 (1)	0·1 (1)	−0·8 (1)	−0·6 (1)
O(8)	−3542 (2)	0298 (3)	−0829 (3)	4·0 (2)	10·5 (3)	4·5 (2)	−1·4 (2)	0·1 (2)	−1·4 (2)
C(1)	1547 (3)	2749 (4)	−2597 (4)	4·8 (3)	4·3 (3)	3·8 (3)	0·0 (2)	0·3 (2)	0·3 (2)
C(2)	2073 (4)	2020 (4)	−2511 (4)	4·4 (3)	4·5 (3)	3·3 (3)	−0·6 (3)	1·3 (2)	−0·2 (2)
C(3)	2170 (3)	1534 (4)	−1619 (4)	3·4 (3)	3·7 (3)	4·2 (3)	0·0 (2)	0·7 (2)	−0·2 (2)
C(4)	1729 (3)	1748 (3)	−0800 (3)	3·0 (2)	2·7 (2)	3·7 (3)	−0·2 (2)	−0·1 (2)	−0·3 (2)
C(5)	1207 (4)	2484 (4)	−0913 (4)	5·2 (3)	5·7 (4)	2·9 (3)	0·9 (3)	1·1 (2)	−0·0 (3)
C(6)	1104 (4)	2990 (5)	−1803 (4)	5·3 (3)	5·5 (3)	4·8 (3)	1·7 (3)	0·8 (3)	1·3 (3)
C(7)	1847 (3)	1185 (3)	0168 (3)	2·4 (2)	4·0 (3)	2·9 (2)	−0·4 (2)	−0·2 (2)	0·1 (2)
C(8)	1384 (3)	1580 (3)	1035 (3)	3·0 (2)	3·2 (2)	2·7 (2)	−0·6 (2)	−0·6 (2)	0·3 (2)
C(9)	1733 (3)	2145 (3)	1769 (3)	2·9 (2)	3·3 (2)	3·1 (2)	−0·7 (2)	−0·3 (2)	0·2 (2)
C(10)	1313 (3)	2517 (3)	2531 (4)	3·7 (3)	3·0 (2)	3·1 (2)	−0·7 (2)	−0·7 (2)	−0·1 (2)
C(11)	0528 (3)	2323 (3)	2574 (3)	3·7 (3)	2·8 (2)	2·2 (2)	−0·2 (2)	0·1 (2)	−0·2 (2)
C(12)	0129 (3)	1755 (3)	1866 (3)	3·0 (2)	2·8 (2)	2·6 (2)	−0·2 (2)	−0·3 (2)	0·2 (2)
C(13)	0580 (3)	1392 (3)	1113 (4)	3·3 (3)	3·2 (2)	2·8 (2)	−0·9 (2)	−0·9 (2)	−0·3 (2)
C(14)	−0746 (3)	1536 (4)	1955 (3)	3·1 (2)	2·7 (2)	2·9 (2)	0·4 (2)	−0·3 (2)	−0·1 (2)
C(15)	−0920 (3)	0907 (3)	2842 (3)	3·1 (2)	3·2 (2)	2·5 (2)	0·0 (2)	−0·3 (2)	−0·0 (2)
C(16)	−0419 (3)	0199 (4)	3186 (4)	3·0 (3)	5·1 (3)	4·1 (3)	0·8 (2)	0·5 (2)	0·8 (2)
C(17)	−0620 (4)	−0384 (4)	3965 (4)	4·7 (3)	4·8 (3)	4·2 (3)	1·2 (3)	−0·2 (2)	1·6 (2)
C(18)	−1315 (3)	−0257 (4)	4408 (3)	4·2 (3)	4·5 (3)	2·9 (2)	0·2 (2)	0·3 (2)	0·3 (2)
C(19)	−1819 (4)	0442 (4)	4091 (4)	3·9 (3)	6·3 (4)	4·5 (3)	1·0 (3)	1·7 (3)	1·3 (3)
C(20)	−1623 (3)	1016 (4)	3311 (4)	3·7 (3)	5·3 (3)	4·4 (3)	1·4 (3)	1·1 (2)	1·3 (3)
C(21)	−1155 (2)	1193 (3)	0996 (3)	2·6 (2)	3·0 (2)	2·6 (2)	0·0 (2)	0·2 (2)	0·4 (2)
C(22)	−1468 (3)	1814 (3)	0278 (3)	2·8 (2)	3·2 (3)	3·2 (2)	−0·5 (2)	−0·1 (2)	0·0 (2)
C(23)	−1878 (3)	1482 (4)	−0566 (3)	3·3 (2)	4·3 (3)	2·7 (2)	0·7 (2)	−0·5 (2)	0·9 (2)
C(24)	−1985 (2)	0531 (4)	−0699 (3)	2·7 (2)	4·2 (3)	2·2 (2)	−0·3 (2)	−0·3 (2)	−0·3 (2)
C(25)	−1689 (2)	−0128 (3)	−0019 (3)	2·3 (2)	3·4 (2)	2·6 (2)	−0·4 (2)	−0·2 (2)	−0·1 (2)
C(26)	−1271 (3)	0232 (4)	0807 (3)	3·0 (2)	3·7 (3)	2·6 (2)	−0·0 (2)	−0·7 (2)	0·8 (2)
C(27)	2792 (4)	3159 (5)	1423 (4)	4·7 (4)	6·3 (4)	4·9 (3)	−2·0 (3)	0·9 (3)	−0·8 (3)
C(28)	3668 (5)	3269 (9)	1542 (8)	4·6 (4)	9·6 (7)	10·1 (6)	−3·2 (5)	0·7 (4)	−0·2 (5)
C(29)	−0231 (3)	3530 (5)	3316 (4)	3·9 (3)	5·3 (4)	4·8 (3)	0·4 (3)	−0·9 (2)	−1·6 (3)
C(30)	−0578 (6)	3804 (9)	4275 (7)	7·6 (5)	8·1 (6)	6·5 (5)	1·9 (5)	0·5 (4)	−2·9 (4)
C(31)	−1036 (3)	3378 (4)	−0099 (5)	4·2 (3)	4·7 (4)	5·4 (3)	0·3 (3)	−0·7 (3)	1·4 (3)
C(32)	−1050 (7)	4355 (6)	0273 (8)	9·4 (6)	4·2 (4)	7·3 (5)	−1·5 (4)	−1·6 (4)	1·0 (4)
C(33)	−3193 (3)	0107 (3)	−1548 (4)	4·1 (3)	3·8 (3)	3·8 (3)	−0·3 (2)	−1·0 (2)	0·5 (2)
C(34)	−3513 (5)	−0293 (7)	−2518 (5)	6·0 (4)	6·9 (5)	5·3 (3)	0·1 (4)	−3·6 (3)	−1·3 (3)

Table 3 (*cont.*)

	x	*y*	*z*	*B*
H(C2)	234 (3)	186 (3)	−297 (3)	2·8 (1)
H(C3)	251 (3)	105 (3)	−156 (3)	3·5 (1)
H(C5)	097 (2)	264 (3)	−045 (3)	1·5 (1)
H(C6)	073 (3)	350 (4)	−181 (4)	5·5 (2)
H(C7)	242 (2)	125 (2)	038 (2)	1·0 (7)
H(C10)	157 (3)	293 (3)	300 (3)	3·8 (1)
H(C13)	033 (2)	101 (2)	063 (3)	1·1 (7)
H(C14)	−095 (2)	210 (2)	204 (2)	−0·4 (7)
H(C16)	005 (3)	014 (3)	293 (3)	4·2 (1)
H(C17)	−027 (3)	−091 (4)	416 (4)	6·6 (1)
H(C19)	−226 (3)	047 (4)	433 (4)	5·6 (2)
H(C20)	−194 (3)	154 (4)	314 (4)	5·6 (1)
H(C23)	−210 (2)	188 (3)	−099 (3)	2·7 (1)
H(C26)	−107 (2)	−016 (3)	124 (3)	1·8 (9)
H1(C28)	391 (5)	307 (6)	222 (7)	12·1 (2)
H2(C28)	401 (4)	266 (5)	151 (5)	8·2 (2)
H3(C28)	383 (6)	377 (7)	145 (8)	12·7 (4)
H1(C30)	−093 (5)	328 (5)	444 (6)	10·2 (3)
H2(C30)	−023 (5)	376 (5)	481 (7)	11·0 (3)
H3(C30)	- 081 (5)	427 (6)	418 (6)	9·5 (3)
H1(C32)	−160 (6)	456 (7)	028 (7)	15·7 (4)
H2(C32)	−095 (4)	443 (5)	091 (5)	8·8 (2)
H3(C32)	−086 (4)	469 (6)	−001 (5)	9·1 (3)
H1(C34)	−366 (5)	021 (6)	−286 (5)	11·0 (3)
H2(C34)	−326 (6)	−085 (7)	−264 (7)	14·1 (4)
H3(C34)	−402 (5)	−043 (5)	−245 (6)	9·2 (2)

weight given to intense reflections and to compensate for non-random errors a term, $(0{\cdot}05I)^2$, was included in the calculation of $\sigma^2(F)=[\sigma^2(I)+(0{\cdot}05I)^2]/(\mathrm{LP})^2$, where LP is the Lorentz-polarization factor.

The intensities of two standard reflections were monitored and found to decrease by 18% for (I) and 5·8% for (II). The observed intensities were corrected for this decrease in a step-wise fashion.

All calculations were carried out on the Berkeley Lawrence Laboratory's CDC 7600 computer with programs furnished by A. Zalkin. The full-matrix least-squares program minimizes the function $\sum w(\Delta F)^2$ where $\Delta F=|F_o|-|F_c|$. The weighting factor w was taken equal to $1/\sigma^2(F)$ where $\sigma(F)=F_o-[F_o^2-\sigma(F_o^2)]^{1/2}$, when $I>2\sigma(I)$ for isomer (I) and $I>\sigma(I)$ for isomer (II) and equal to zero otherwise. Scattering factors for all atoms except H were taken from Cromer & Waber (1965). The H scattering factors were from Stewart, Davidson & Simpson (1965).

Determination of the structure

The structures of both isomers were determined by means of a phase-determining program (Maddox & Maddox, 1965) and Fourier synthesis. Least-squares refinement of the positional parameters of the 44 heavy atoms with anisotropic temperature factors for (I) gave an R_1 index of 0·117 for 2590 reflections ($R_1=0{\cdot}146$ for all 3383 reflections) where R_1 is defined as $\sum||F_o|-|F_c||/\sum|F_o|$. In the final cycle of least-squares refinement all parameter shifts were less than $0{\cdot}1\sigma$. Because the data were comparatively poor for (I) owing to radiation damage the refinement was discontinued.

The least-squares refinement of the data for (II) resulted in an R_1 index of 0·063 for 44 heavy atoms with anisotropic temperature factors. The addition of 26 hydrogen atoms, with isotropic temperature factors, reduced R_1 to the final value of 0·043 when reflections with $I\le(\sigma I)$ were excluded from the least-squares refinement and 0·055 for all data. R_2, defined as $[\sum w|\Delta F|^2/\sum w|F_o|^2]^{1/2}$, is 0·046; the standard deviation of an observation of unit weight is 1·27.

The final positional and thermal parameters and their estimated standard deviations are given in Table 2 for (I) and Table 3 for (II).*

Table 4. *Dihedral angles between the planes A, B, C and D (Fig. 2), and the planes E*[C(27), C(28), O(1), O(2)], *F*[C(29), C(30), O(3), O(4)], *G*[C(31), C(32), O(5), O(6)], *H*[C(33), C(34), O(7), O(8)], *I*[C(7), C(7′), C(14), C(14′)]

Planes	(I)	(II)	Planes	(I)	(II)
A–B	86·7°	77·7°	*B–D*	88·4°	85·9°
B–C	−84·1	85·7	*B–E*	84·6	−82·3
C–D	83·1	89·0	*B–F*	72·6	87·8
A–C	−9·3	25·3	*D–G*	84·0	62·4
A–D	82·6	64·7	*D–H*	43·2	88·4
A–I	79·4	89·6	*C–I*	88·5	80·8
B–I	−8·8	−13·5	*D–I*	84·5	−86·9

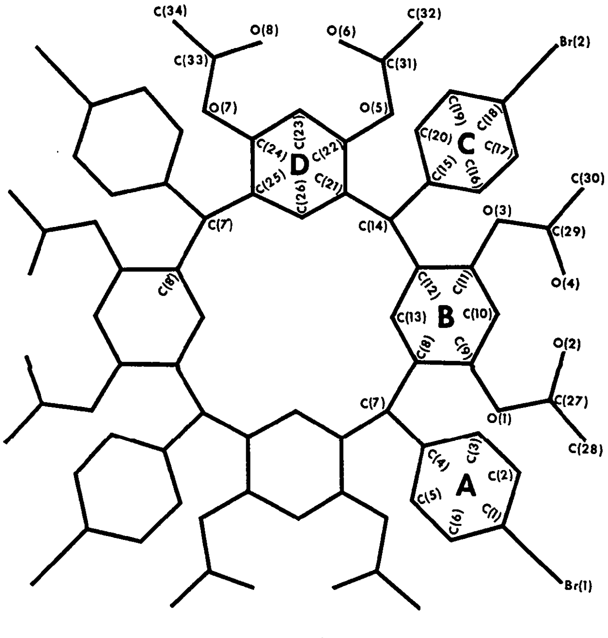

Fig. 2. A schematic drawing of the condensation tetramers showing the atom numbering system used and the designation of the benzene rings.

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* A list of structure factors and a table of bond angles for both isomers have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31310 (31 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion of the structures

A schematic drawing of the octaacetate ester of the condensation tetramer, with the atom numbering system used in this investigation, is shown in Fig. 2. The molecular structure of (I) is illustrated in the stereoscopic drawing, Fig. 3, produced with the *ORTEP* program (Johnson, 1965).

The configuration of the benzene rings and the arrangement of the four *p*-bromophenyl units on one side of the molecule are the same as observed by Nilsson (1968) for the octabutyrate ester. (I) has a twofold axis of symmetry, and a comparison of Fig. 3 with Fig. 1 in Nilsson's paper shows that an important reason for the lack of molecular symmetry in the butyrate ester is due to the two end C atoms of the butyrate chain.

The configuration of the benzene rings in (II) is shown in Fig. 4 (and schematically in Fig. 1). This

Table 5. *Interatomic distances in the octaacetate derivatives of* (I) *and* (II)

Estimated standard deviations in parentheses.

	(I)	(II)		(I)	(II)
Br(1)–C(1)	1·93 (2) Å	1·887 (5) Å	C(8)—C(13)	1·41 (2) Å	1·396 (6) Å
Br(2)–C(18)	1·86 (2)	1·898 (5)	C(9)—C(10)	1·38 (2)	1·367 (6)
O(1)–C(9)	1·38 (2)	1·405 (5)	C(10)–C(11)	1·39 (2)	1·361 (6)
O(1)–C(27)	1·35 (2)	1·361 (7)	C(11)–C(12)	1·37 (2)	1·388 (6)
O(2)–C(27)	1·20 (2)	1·183 (7)	C(12)–C(13)	1·41 (2)	1·384 (6)
O(3)–C(11)	1·43 (2)	1·401 (5)	C(12)–C(14)	1·56 (2)	1·520 (6)
O(3)–C(29)	1·32 (2)	1·360 (6)	C(14)–C(15)	1·56 (2)	1·517 (6)
O(4)–C(29)	1·21 (2)	1·190 (7)	C(14)–C(21)	1·52 (2)	1·511 (6)
O(5)–C(22)	1·40 (2)	1·398 (5)	C(15)–C(16)	1·40 (2)	1·372 (6)
O(5)–C(31)	1·24 (3)	1·350 (6)	C(15)–C(20)	1·36 (2)	1·373 (7)
O(6)–C(31)	1·29 (2)	1·202 (7)	C(16)–C(17)	1·40 (2)	1·376 (7)
O(7)–C(24)	1·39 (1)	1·409 (5)	C(17)–C(18)	1·41 (3)	1·348 (7)
O(7)–C(33)	1·39 (3)	1·369 (6)	C(18)–C(19)	1·33 (2)	1·358 (7)
O(8)–C(33)	1·19 (2)	1·178 (6)	C(19)–C(20)	1·44 (2)	1·367 (8)
C(1) –C(2)	1·36 (2)	1·361 (7)	C(21)–C(22)	1·43 (2)	1·385 (6)
C(1) –C(6)	1·37 (3)	1·364 (7)	C(21)–C(26)	1·39 (2)	1·383 (6)
C(2) –C(3)	1·39 (2)	1·377 (7)	C(22)–C(23)	1·35 (2)	1·379 (6)
C(3) –C(4)	1·39 (2)	1·382 (7)	C(23)–C(24)	1·38 (2)	1·355 (7)
C(4) –C(5)	1·39 (2)	1·362 (7)	C(24)–C(25)	1·41 (2)	1·380 (6)
C(4) –C(7)	1·53 (2)	1·522 (6)	C(25)–C(26)	1·39 (2)	1·379 (6)
C(5) –C(6)	1·41 (2)	1·390 (8)	C(27)–C(28)	1·54 (2)	1·494 (10)
C(7) –C(8)	1·52 (2)	1·525 (6)	C(29)–C(30)	1·50 (3)	1·481 (10)
C(7) –C(25)	1·51 (2)	1·519 (6)	C(31)–C(32)	1·48 (3)	1·461 (10)
C(8) –C(9)	1·38 (2)	1·376 (6)	C(33)–C(34)	1·44 (2)	1·492 (8)

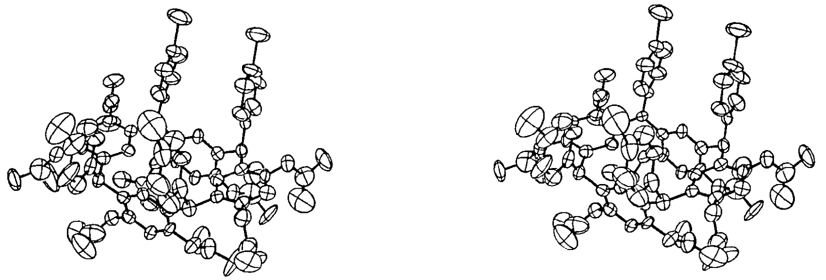

Fig. 3. A stereoscopic view of (I). The thermal ellipsoids are drawn at the 50% level.

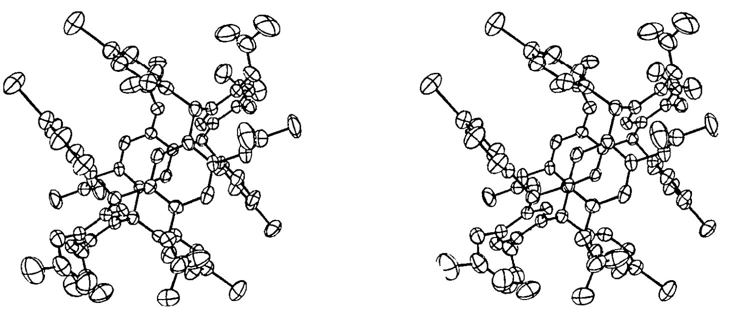

Fig. 4. A stereoscopic view of (II). The thermal ellipsoids are drawn at the 50% level.

structure has, like (I), two pairs of resorcinol units approximately perpendicular to each other; but, in contrast to (I), the two pairs of *p*-bromophenyl units are on opposite sides of the molecule. The planes of the *p*-bromophenyl units are nearly parallel to each other, and approximately perpendicular to the planes of both pairs of resorcinol units.

In (I) the two vertically oriented resorcinol units (Fig. 1) and the two pairs of *p*-bromophenyl units have a *cis* configuration; in (II) they are *trans*. The octaacetate molecule (II) has a center of symmetry. The maximum deviation from planarity of the benzene rings in both isomers is 0·011 Å. The Br atoms are approximately 0·1 Å out of the plane of the benzene ring to which it is bonded in (I), and 0·04 Å in (II). The dihedral angles between the planes *A*, *B*, *C* and *D* (Fig. 2), the planes formed by the ester groups, and the plane formed by the four condensation centers are shown in Table 4 for both isomers. The angles between the three phenyl groups bonded to the same condensation center fall between 80 and 90°; their average value is 82·7 in (I) and 86·9° in (II). The dihedral angle between the two *p*-bromophenyl rings, *A* and *C* (Fig. 2), is 12 in (I) and 25° in (II).

Both isomers have two pairs of resorcinol units with nearly parallel planes. The pairs are distinguished by the fact that one pair lies (nearly) in the same plane and the other pair in parallel planes. The two pairs are also distinguished by the fact that the keto O atoms of the ester groups are on the same side of the resorcinol plane for the pair which lies in the same plane, but on the opposite side of the resorcinol plane for the other pair. This arrangement of the keto O atoms also occurs in the butyrate ester (Nilsson, 1968).

The bond distances for both (I) and (II) are listed in Table 5, with the estimated standard deviations given in parentheses. The agreement between these bond distances and those published by Nilsson (1968) for the octabutyrate ester is satisfactory. The bond distances are considerably more consistent for (II) than for (I). For example, the two C–Br distances in (I) vary by 0·07 Å (3σ), but only by 0·011 Å in (II). The O(5)–C(31) distance of 1·24 Å in (I) is shorter by 4σ than the average value while the O(6)–C(31) distance of 1·29 Å is larger than the average value by 5σ. The corresponding bond distances in (II) are normal.

Tables of bond angles for both isomers have been deposited.*

The thermal parameters are appreciably smaller for (II) than for (I). This is particularly true for the Br atoms and the carboxyl O atoms. The comparatively large values for (I) are, in part, a reflection of the radiation damage observed for this isomer.

During the least-squares refinement of the isomer (II) data, the H parameters were allowed to vary independently. As a result, the thermal parameters for H(C14) became slightly negative and those for the methyl H atoms quite large, presumably because of methyl torsion.

In the synthesis of the condensation tetramers the yield of (II) is almost eight times that of (I). The stability of (II) to X-ray irradiation is also about three times greater than (I). There is no obvious relationship between these two observations and the configuration of the isomers. The minimum Br–Br distance in (I) is 4·16 Å which is greater than twice the van der Waals radius of Br (3·90 Å) (Pauling, 1960); consequently, the instability of (I) is not due to steric hindrance between Br atoms.

There are no intermolecular bonds in the crystal; the only attractive forces between molecules arise from van der Waals interactions.

We wish to thank Dr A. Zalkin for the use of his computer programs.

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* See previous footnote.

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