39° (absolute values). The lactone rings are much less puckered. That of (1) is close to the twist form. Its largest intra-annular torsion angle is C(9)C(6)C(11)-
O(10) with -12-2 (7) °. The lactone ring of (2) is almost flat. Its largest torsional angle, C(10)O(10)-
C(11)C(6), is -3-7 (1)°.

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Conformational Effects in Methoxybenzenes Caused by Ortho Disubstitution. I.
Pentachloromethoxybenzene

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(Received 9 January 1987; accepted 18 May 1987)

Abstract. C7H3Cl5O, Mr= 280.37, monoclinic, P21,
a = 8.636 (3), b = 3.935 (5), c = 16.925 (7) Å, β =
120.30 (5)°, V = 496.6 Å3, Z = 2, Dc = 1.87 Mg m-3,
λ(Mo Kα) = 0.7107 Å, μ = 1.42 mm-1, F(000) = 276,
T = 296 K, final R = 0.054 for 775 unique observed
reflections. Ortho disubstitution forces the methoxy

group to move out of the benzene plane, so that the
methoxy C atom [C(7)] is 1.182 (13) Å above and the
methoxy O atom [O(1)] 0.135 (9) Å below the cal-
culated least-squares plane [C(1)-C(6)]. The angle
C(7)-O(1)-C(1) is 112.2(9)°. The rest of the
molecule is nearly planar: maximum distance from the
least-squares plane is 0.037 (4) Å [C1(2)].

Introduction. Chlorinated methoxybenzenes (anisoles)
and 1,2-dimethoxybenzenes (veratroles) have been
shown to be formed by bacterial biomethylation of
chlorinated phenols, 1,2-benzenediols (pyrocatechols)
and 2-methoxyphenols (guaiacols), which are produced
in chlorobleaching processes in kraft pulp mills
(Knuutinen, 1984). These same compounds are con-
sidered as potential off-flavour compounds and are
frequently detected in environmental samples
(Paasivirta et al., 1983).

Quantum-chemical and spectroscopic studies (An-
derson, Kollman, Domelsmith & Houk, 1979;
Koehmainen & Knuutinen, 1983) have revealed that
ortho disubstitution causes drastic changes in the
spatial arrangement of the methoxy group. Methoxy-
benzenes lacking ortho disubstitution are planar, but
when ortho disubstitution occurs the methoxy group
moves out of the benzene plane.

The purpose of our study was to solve the molecular
structure of pentachloromethoxybenzene and determine
the degree of out-of-plane displacement of the methoxy
group caused by ortho disubstitution.

Experimental. Colourless crystals (m.p. 377–379 K)
synthesized by refluxing pentachlorophenol with
potassium carbonate and methyl iodide in acetone
(Knuutinen & Korhonen, 1987), 0.40 × 0.50 ×
0.65 mm, mounted on a glass fibre; Enraf–Nonius
CAD-4 diffractometer; graphite-monochromatized
Mo Kα; ω–2θ method; lattice parameters from 25
reflections with 9 < 0< 17°; two standard reflections
measured every hour, no loss of intensity; 1000
reflections (h: 0–10, k: 0–4, l: −20–20) with 0 < 25°,
1000 independent, 775 with I > 3σ(I); Lp correction;
empirical absorption correction (Walker & Stuart,
1983), correction factors: max. = 1.195 and min.
= 0.934; direct methods; refinement by full-matrix
least-squares method using unit weights and Fς; all
non-H atoms anisotropic; all H atoms calculated and
used as riding atoms in final refinement (C–H distance
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Table 1. Fractional coordinates and equivalent isotropic thermal parameters for pentachloromethoxybenzene with e.s.d.'s in parentheses

\[
B_{eq} = a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma B(1,2) + ac\cos\alpha B(1,3) + bc\cos\beta B(2,3).
\]

<table>
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<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B_{eq}(\text{\AA}^2)</th>
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<td>Cl(1)</td>
<td>0.6345</td>
<td>0.921</td>
<td>0.9554</td>
<td>4.91 (8)</td>
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<td>Cl(2)</td>
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<td>Cl(3)</td>
<td>0.7356 (4)</td>
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<td>Cl(4)</td>
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<td>0.576 (1)</td>
<td>0.5409 (2)</td>
<td>6.20 (10)</td>
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<tr>
<td>Cl(5)</td>
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<td>0.879 (2)</td>
<td>0.7475 (5)</td>
<td>4.6 (2)</td>
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<tr>
<td>C(1)</td>
<td>0.392 (1)</td>
<td>0.991 (3)</td>
<td>0.7787 (6)</td>
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<tr>
<td>C(2)</td>
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<td>0.882 (3)</td>
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<td>C(3)</td>
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<td>C(4)</td>
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<td>0.695 (4)</td>
<td>0.7196 (6)</td>
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<td>C(5)</td>
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<td>0.810 (4)</td>
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<td>0.6859 (7)</td>
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<tr>
<td>C(7)</td>
<td>0.1688 (4)</td>
<td>0.974 (4)</td>
<td>0.8206 (2)</td>
<td>5.1 (3)</td>
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Table 2. Bond distances (\text{\AA}) and angles (\textdegree) in pentachloromethoxybenzene with e.s.d.'s in parentheses

<table>
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<tr>
<th></th>
<th>C(2)</th>
<th>C(3)</th>
<th>C(4)</th>
<th>C(5)</th>
<th>C(6)</th>
<th>C(7)</th>
<th>C(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(1)</td>
<td>1.698 (10)</td>
<td>1.714 (9)</td>
<td>1.727 (13)</td>
<td>1.704 (11)</td>
<td>1.711 (9)</td>
<td>1.717 (13)</td>
<td>1.698 (10)</td>
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<td>C(2)</td>
<td>1.368 (11)</td>
<td>1.382 (14)</td>
<td>1.376 (15)</td>
<td>1.398 (13)</td>
<td>1.392 (19)</td>
<td>1.402 (18)</td>
<td>1.368 (11)</td>
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<tr>
<td>C(3)</td>
<td>1.212-2 (9)</td>
<td>1.219 (1)</td>
<td>1.188-8 (8)</td>
<td>1.222 (1)</td>
<td>1.196-6 (7)</td>
<td>1.199-8 (9)</td>
<td>1.212-2 (9)</td>
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<tr>
<td>C(4)</td>
<td>1.20-2 (9)</td>
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<td>1.20-2 (9)</td>
<td>1.220 (1)</td>
<td>1.198-6 (8)</td>
<td>1.211 (1)</td>
<td>1.20-2 (9)</td>
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<td>C(5)</td>
<td>1.199-6 (8)</td>
<td>1.220-2 (9)</td>
<td>1.220-2 (9)</td>
<td>1.199-8 (9)</td>
<td>1.211 (1)</td>
<td>1.20 (1)</td>
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<tr>
<td>C(6)</td>
<td>1.21-2 (9)</td>
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<td>1.20-2 (9)</td>
<td>1.220 (1)</td>
<td>1.198-6 (8)</td>
<td>1.211 (1)</td>
<td>1.21-2 (9)</td>
</tr>
<tr>
<td>C(7)</td>
<td>1.493 (13)</td>
<td>1.493 (13)</td>
<td>1.493 (13)</td>
<td>1.493 (13)</td>
<td>1.493 (13)</td>
<td>1.493 (13)</td>
<td>1.493 (13)</td>
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</table>

Discussion. The atomic coordinates are listed in Table 1 and bond distances and angles are given in Table 2. A view of the molecule and the numbering scheme are shown in Fig. 1. The stereoview of the packing is presented in Fig. 2.

Bond distances and angles are normal. Refinement of H atoms with isotropic thermal parameters and free coordinates was not successful. The H atoms had to be treated as riding atoms in the final refinement with fixed C–H distance. The planarity of methoxybenzene lacking ortho disubstitution has been confirmed by \textit{ab initio} STO-3G calculations performed on various methoxybenzenes (Anderson et al., 1979). NMR studies of ortho-disubstituted methoxybenzenes (Kolehmainen & Knuutinen, 1983) have indicated that in solution the methoxy group tends to prefer perpendicular arrangement. A literature survey of the methoxy-group bond distances in unsubstituted methoxybenzenes (Anderson et al., 1979) gives the distances between the methoxy C and O atoms and between the O atom and the benzene C atom as 1.43 (2) and 1.37 (2) \text{\AA}, respectively. The longer methoxy C(7)–O(1) distance, 1.493 (13) \text{\AA}, observed in our study is probably caused by steric repulsions between the methoxy C atom and the Cl atoms in ortho positions. According to Sakurai (1962), pentachlorophenol has a planar structure, the largest deviations from the least-squares plane being 0.056 \text{\AA} for Cl(3) and –0.020 \text{\AA} for the phenolic O atom. The out-of-plane displacement of the phenolic O atom is very small compared with that of the methoxy O atom in pentachloromethoxybenzene [deviation –0.135 (9) \text{\AA}]. Steric repulsions that cause lengthening of the methoxy C(7)–O(1) distance also affect the O atom by forcing it to move further below the benzene plane.

The financial support of the Academy of Finland and the Maj and Tor Nessling Foundation (to JK) is gratefully acknowledged.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44062 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. \textit{ORTEP} plot (Johnson, 1976) and numbering scheme for pentachloromethoxybenzene. Thermal ellipsoids are shown at the 50% probability level.

Fig. 2. Stereoview of packing for pentachloromethoxybenzene. The a axis is horizontal and the c axis vertical.

Structure of Two Isomers of Perhydro-5,8-epoxy-6,7-dimethoxynaphthalene-1,4-dione

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Abstract. C_{12}H_{16}O_{5}, M_r = 240.26. cis-transoid form: triclinic, P1, a = 9.14 (2), b = 9.70 (2), c = 7.80 (1) Å, α = 110.5 (3), β = 109.5 (3), γ = 101.7 (3)°, V = 569 (3) Å^{3}, Z = 2, D_x = 1.402 (7) g cm^{-3}, λ = 0.7107 Å, μ(Mo Ka) = 1.021 cm^{-1}, F(000) = 256, 1172 unique observed reflections. cis-cisoid form: orthorhombic, P2_{1}2_{1}2_{1}, a = 7.808 (10), b = 8.840 (7), c = 16.662 (11) Å, V = 1150 (2) Å^{3}, Z = 4, D_x = 1.388 (2) g cm^{-3}, λ = 0.7107 Å, μ(Mo Ka) = 1.010 cm^{-1}, F(000) = 512, 1039 unique observed reflections. Room temperature. The structures were solved by direct methods. The final R factors were 0.051 and 0.066 for the cis-transoid and cis-cisoid forms, respectively.

Introduction. Eugster et al. (Hofmann, Wyrsch-Walraf, Iten & Eugster, 1979) have reported that thermal Diels-Alder reaction between 3,4-dimethoxyfuran (1) and benzoquinone (2) leads exclusively to the endo-

adduct (3). Under high-pressure conditions (10–20 kbar), both endo- and exo-adducts (3) and (4) are formed (Jurczak, Koziuk, Tkacz & Eugster, 1983). Hydrogenation of this mixture afforded the tetrahydro derivatives (5) and (6) which were separated by column chromatography to give pure, stable crystals of both title compounds.