

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 $-12.2(7)^\circ$. The lactone ring of (2) is almost flat. Its largest torsional angle, C(10)O(10)-C(11)C(6), is $-3.7(1)^\circ$.

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

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Abstract. C₇H₃Cl₅O, $M_r = 280.37$, monoclinic, $P2_1$, $a = 8.636(3)$, $b = 3.935(5)$, $c = 16.925(7)$ Å, $\beta = 120.30(5)^\circ$, $V = 496.6$ Å³, $Z = 2$, $D_x = 1.87$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.42$ 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 calculated 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 [Cl(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 considered as potential off-flavour compounds and are frequently detected in environmental samples (Paasivirta *et al.*, 1983).

Quantum-chemical and spectroscopic studies (Anderson, Kollman, Domelsmith & Houk, 1979; Kolehmainen & Knuutinen, 1983) have revealed that

ortho disubstitution causes drastic changes in the spatial arrangement of the methoxy group. Methoxybenzenes 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 $K\alpha$; ω - 2θ method; lattice parameters from 25 reflections with $9 < \theta < 17^\circ$; two standard reflections measured every hour, no loss of intensity; 1000 reflections (h : 0→10, k : 0→4, l : -20→20) with $\theta < 25^\circ$, 1000 independent, 775 with $I > 3\sigma(I)$; 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 F^2 s; all non-H atoms anisotropic; all H atoms calculated and used as riding atoms in final refinement (C-H distance

Table 1. Fractional coordinates and equivalent isotropic thermal parameters for pentachloromethoxybenzene with *e.s.d.*'s in parentheses

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

| | x | y | z | $B_{\text{eq}}(\text{\AA}^2)$ |
|-------|------------|-----------|------------|-------------------------------|
| Cl(1) | 0.6345 | 0.921 | 0.9554 | 4.91 (8) |
| Cl(2) | 0.8767 (3) | 0.579 (1) | 0.8906 (2) | 4.42 (7) |
| Cl(3) | 0.7356 (4) | 0.504 (1) | 0.6820 (2) | 4.89 (7) |
| Cl(4) | 0.3573 (4) | 0.766 (1) | 0.5409 (2) | 6.20 (10) |
| Cl(5) | 0.1185 (4) | 1.107 (1) | 0.6090 (2) | 5.61 (9) |
| O(1) | 0.2940 (9) | 1.170 (2) | 0.8075 (5) | 4.6 (2) |
| C(1) | 0.392 (1) | 0.991 (3) | 0.7787 (6) | 2.9 (2) |
| C(2) | 0.561 (1) | 0.882 (3) | 0.8420 (6) | 2.9 (2) |
| C(3) | 0.668 (1) | 0.728 (4) | 0.8119 (6) | 3.2 (2) |
| C(4) | 0.604 (1) | 0.695 (4) | 0.7196 (6) | 3.5 (3) |
| C(5) | 0.433 (1) | 0.810 (4) | 0.6549 (7) | 4.1 (3) |
| C(6) | 0.328 (1) | 0.959 (3) | 0.6859 (7) | 3.3 (3) |
| C(7) | 0.1688 (4) | 0.947 (4) | 0.8206 (2) | 5.1 (3) |

Table 2. Bond distances (\AA) and angles ($^\circ$) in pentachloromethoxybenzene with *e.s.d.*'s in parentheses

| | | | |
|-----------------|------------|-----------------|------------|
| Cl(1) C(2) | 1.698 (10) | C(1) C(2) | 1.368 (11) |
| Cl(2) C(3) | 1.714 (9) | C(1) C(6) | 1.382 (14) |
| Cl(3) C(4) | 1.727 (13) | C(3) C(4) | 1.376 (15) |
| Cl(4) C(5) | 1.704 (11) | C(4) C(5) | 1.398 (13) |
| Cl(5) C(6) | 1.711 (9) | C(5) C(6) | 1.392 (19) |
| O(1) C(1) | 1.369 (15) | C(2) C(3) | 1.402 (18) |
| O(1) C(7) | 1.493 (13) | | |
| C(1) O(1) | 112.2 (9) | Cl(4) C(5) C(6) | 121.2 (7) |
| O(1) C(1) C(2) | 119 (1) | Cl(4) C(5) C(4) | 120 (2) |
| O(1) C(1) C(6) | 118.9 (8) | Cl(5) C(6) C(1) | 120.0 (9) |
| C(2) C(1) C(6) | 122 (1) | C(1) C(6) C(5) | 120.0 (8) |
| Cl(1) C(2) C(1) | 120.1 (9) | C(1) C(6) C(5) | 120.1 (8) |
| Cl(1) C(2) C(3) | 120.7 (6) | C(4) C(5) C(6) | 118 (1) |
| C(1) C(2) C(3) | 119.2 (9) | Cl(3) C(4) C(3) | 119.9 (8) |
| Cl(2) C(3) C(2) | 119.6 (7) | Cl(3) C(4) C(5) | 118.8 (9) |
| Cl(2) C(3) C(4) | 121 (1) | C(3) C(4) C(5) | 121 (1) |
| C(2) C(3) C(4) | 119.6 (8) | | |

fixed 1.00 \AA); 130 parameters; max. shift/ σ = 0.08 on final cycle; R = 0.054, wR = 0.062, S = 1.135; final difference map with no features greater than 0.34 (11) $e \text{\AA}^{-3}$; scattering factors from *International Tables for X-ray Crystallography* (1974); computer programs *MULTAN11/82* (Main *et al.*, 1982), *SDP* (Frenz, 1978) and *ORTEPII* (Johnson, 1976).*

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

* 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.

treated as riding atoms in the final refinement with fixed C—H distance. The planarity of methoxybenzene lacking *ortho* disubstitution has been confirmed by *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) \AA , respectively. The longer methoxy C(7)—O(1) distance, 1.493 (13) \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 \AA for Cl(3) and -0.020\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) \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.

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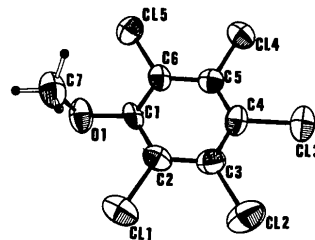


Fig. 1. ORTEP plot (Johnson, 1976) and numbering scheme for pentachloromethoxybenzene. Thermal ellipsoids are shown at the 50% probability level.

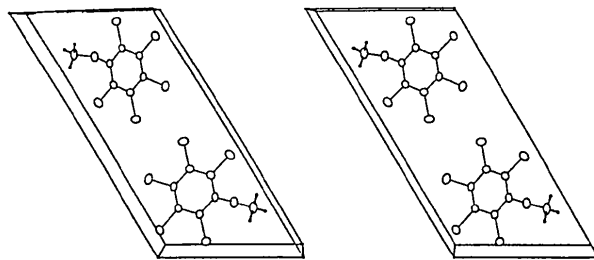


Fig. 2. Stereoview of packing for pentachloromethoxybenzene. The *a* axis is horizontal and the *c* axis vertical.

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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, $P\bar{1}$, $a = 9.14$ (2), $b = 9.70$ (2), $c = 7.80$ (1) Å, $\alpha = 110.5$ (3), $\beta = 109.5$ (3), $\gamma = 101.7$ (3)°, $V = 569$ (3) Å³, $Z = 2$, $D_x = 1.402$ (7) g cm⁻³, $\lambda = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 1.021$ cm⁻¹, $F(000) = 256$, 1172 unique observed reflections. *cis-cisoid* form: orthorhombic, $P2_12_12_1$, $a = 7.808$ (10), $b = 8.840$ (7), $c = 16.662$ (11) Å, $V = 1150$ (2) Å³, $Z = 4$, $D_x = 1.388$ (2) g cm⁻³, $\lambda = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 1.010$ 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, Wyrsh-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, Koźluk, 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.

