

# Crystal and Molecular Structure of 2,3-Dichloro-4,5-dimethoxy-1-(2,3,4-trichloro-6-methoxyphenoxy)benzene: a Derivative of the Oxidative Coupling Product of 4,5,6-Trichloroguaiacol

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Bleached Kraft Mill Effluents (BKME) and their effects on aquatic organisms have recently been investigated.<sup>1</sup> The toxic effect of BKME has partly been ascribed to chlorinated phenolic compounds, mainly chloroguaiacols and chlorocatechols.<sup>2</sup> Phenolic compounds readily undergo oxidative coupling to form di-, tri- and poly-mers.<sup>3</sup> However, substituents like chlorine increase the likelihood of such a reaction stopping at the dimer or oligomer stage. Such compounds may be of interest because they are better lipophiles than the monomeric phenol and hence probably have a greater tendency to accumulate in the biosphere. Compound, **2**, was prepared from 4,5,6-trichloroguaiacol during a study of quinonoid dimers derived from chlorinated phenolic compounds occurring in BKME. It was obtained from the primary oxidation product **1** by reduction and subsequent methylation.<sup>4</sup> A tentative structure for **2** was proposed, essentially on the basis of the fragmentation patterns obtained by GC–EIMS of compounds **3** and **4**; but since no reference material is available and only one isomer of the primary coupling product **1** is formed in substantial yield, crystallographic data were crucial in determining the structure.

## Experimental

Crystals of the title compound were formed by recrystallization from methanol–water (20:1).<sup>4</sup> Systematic absences  $h0l$ :  $l = 2n+1$  and  $0k0$ :  $k = 2n+1$  indicated the space-group  $P2_1/c$ . Lattice parameters were refined by least-squares calculations based on setting angles of 24 selected reflections. Crystal data are given in Table 1. Intensities were measured in the  $\omega$ -scan mode at a speed of  $0.004$ – $0.03^\circ\text{s}^{-1}$  and a basic scan width of  $1.05^\circ$ . The background was measured at each end of the scan interval. Three standard reflections measured every 120 min during the data collection showed no sign of crystal deterioration. The

data were corrected for Lorentz and polarization effects and also for absorption using numerical integration. The scattering factors were those included in SHELX.<sup>5</sup>

The structure was determined by direct methods with the program SHELXS,<sup>6</sup> and the model obtained was refined by full-matrix least-squares calculations with the program SHELX.<sup>5</sup> All non-hydrogen atoms but one could be located in the first electron density map. The remaining atom, [C(15)] could be located after a few cycles of least-squares calculations and a following difference Fourier map. One hydrogen atom, [H(1)], also appeared in this map. All hydrogen positions were, however, calculated and allowed to ride at a distance of  $1.08 \text{ \AA}$  on the carbon atoms

Table 1. Crystal data and structural parameters.

Compound	$\text{C}_{15}\text{H}_{11}\text{Cl}_5\text{O}_4$
Diffractometer	Siemens STOE/AED2
Radiation	$\text{Mo } K_\alpha$ ( $\lambda = 0.7107 \text{ \AA}$ )
Space group	$P2_1/c$
$a/\text{\AA}$	8.811(4)
$b/\text{\AA}$	8.410(4)
$c/\text{\AA}$	24.67(1)
$\beta/^\circ$	99.91(3)
$V/\text{\AA}^3$	1801(2)
$Z$	4
$F(000)$	872
$\mu(\text{Mo } K_\alpha)/\text{cm}^{-1}$	7.47
$D_{\text{calc}}/\text{g cm}^{-3}$	1.595(2)
Crystal dimensions/mm	$0.08 \times 0.10 \times 0.24$
Scan mode	$\omega$
Maximum value of $2\theta/^\circ$	40
Measured reflections	1840
Unique observed reflections [ $I \geq 3\sigma(I)$ ]	738
Number of refined parameters	122
Transmission factors	0.90–0.94
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.041
$R_w = [\sum w( F_o  -  F_c )^2 / \sum w F_o ^2]^{1/2}$	0.037
Goodness of fit	1.89

Table 2. Fractional atomic coordinates and  $U_{eq}$  ( $\text{\AA}^2$ ). Estimated standard deviations are given in parentheses.

Atom	x	y	z	$U_{eq}/U_{iso}$
Cl(1)	0.7393(3)	1.1201(4)	0.1266(1)	0.087(2)
Cl(2)	0.9794(3)	0.6332(4)	0.0819(1)	0.093(2)
Cl(3)	1.0628(3)	0.4010(4)	0.1831(2)	0.111(2)
Cl(4)	0.4382(4)	1.3253(4)	0.1137(1)	0.101(2)
Cl(5)	0.1268(3)	1.1750(4)	0.0544(1)	0.095(2)
O(1)	0.6974(7)	0.8025(8)	0.0794(3)	0.063(2)
O(2)	0.4363(8)	0.6771(8)	0.0270(3)	0.071(2)
O(3)	0.8317(8)	0.3860(10)	0.2536(3)	0.087(2)
O(4)	0.5755(8)	0.5590(8)	0.2453(3)	0.074(2)
C(1)	0.564(1)	0.889(1)	0.0731(4)	0.052(3)
C(2)	0.862(1)	0.613(1)	0.1302(4)	0.051(3)
C(3)	0.629(1)	0.687(1)	0.1627(4)	0.048(3)
C(4)	0.566(1)	1.044(1)	0.0931(4)	0.058(3)
C(5)	0.897(1)	0.513(1)	0.1749(4)	0.057(3)
C(6)	0.433(1)	1.135(1)	0.0875(4)	0.059(3)
C(7)	0.665(1)	0.584(1)	0.2061(4)	0.054(3)
C(8)	0.297(1)	1.069(1)	0.0609(4)	0.059(3)
C(9)	0.804(1)	0.496(1)	0.2129(4)	0.060(3)
C(10)	0.300(1)	0.600(1)	-0.0005(4)	0.078(4)
C(11)	0.430(1)	0.640(1)	0.2388(4)	0.088(4)
C(12)	0.426(1)	0.829(1)	0.0458(4)	0.058(3)
C(13)	0.726(1)	0.704(1)	0.1241(4)	0.049(3)
C(14)	0.292(1)	0.917(1)	0.0396(3)	0.054(3)
C(15)	0.886(1)	0.448(2)	0.3061(5)	0.128(5)

$$^a(U_{eq} = \frac{1}{3} \sum \Sigma U_{ii}).$$

Table 3. Bond lengths ( $\text{\AA}$ ) with estimated standard deviations = 0.01  $\text{\AA}$ .

C(1)–O(1)	1.37	C(1)–C(4)	1.39
C(1)–C(12)	1.38	C(2)–C(5)	1.38
C(2)–C(13)	1.41	C(2)–Cl(2)	1.72
C(3)–C(7)	1.37	C(3)–C(13)	1.43
C(4)–C(6)	1.39	C(4)–Cl(1)	1.72
C(5)–C(9)	1.35	C(5)–Cl(3)	1.72
C(6)–C(8)	1.38	C(6)–Cl(4)	1.72
C(7)–C(9)	1.42	C(7)–O(4)	1.36
C(8)–C(14)	1.38	C(8)–Cl(5)	1.73
C(9)–O(3)	1.35	C(10)–O(2)	1.42
C(11)–O(4)	1.43	C(12)–C(14)	1.37
C(12)–O(2)	1.37	C(13)–O(1)	1.37
C(15)–O(3)	1.40		

Table 4. Bond angles ( $^\circ$ ) with estimated standard deviations =  $1^\circ$ .

C(13)–O(1)–C(1)	117	C(12)–O(2)–C(10)	119
C(15)–O(3)–C(9)	115	C(11)–O(4)–C(7)	117
C(4)–C(1)–O(1)	120	C(12)–C(1)–O(1)	122
C(12)–C(1)–C(4)	118	C(5)–C(2)–Cl(2)	123
C(13)–C(2)–Cl(2)	118	C(13)–C(2)–C(5)	119
C(13)–C(3)–C(7)	121	C(1)–C(4)–Cl(1)	118
C(6)–C(4)–Cl(1)	120	C(6)–C(4)–C(1)	122
C(2)–C(5)–Cl(3)	120	C(9)–C(5)–Cl(3)	118
C(9)–C(5)–C(2)	123	C(4)–C(6)–Cl(4)	121
C(8)–C(6)–Cl(4)	121	C(8)–C(6)–C(4)	118
C(3)–C(7)–O(4)	125	C(9)–C(7)–O(4)	115
C(9)–C(7)–C(3)	120	C(6)–C(8)–Cl(5)	121
C(14)–C(8)–Cl(5)	118	C(14)–C(8)–C(6)	121
C(5)–C(9)–O(3)	122	C(7)–C(9)–O(3)	119
C(7)–C(9)–C(5)	118	C(1)–C(12)–O(2)	114
C(14)–C(12)–O(2)	125	C(14)–C(12)–C(1)	122
C(2)–C(13)–O(1)	117	C(3)–C(13)–O(1)	124
C(3)–C(13)–C(2)	119	C(12)–C(14)–C(8)	119

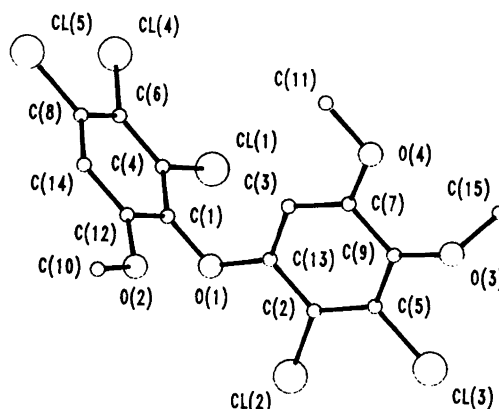


Fig. 1. Numbering scheme of the molecule.

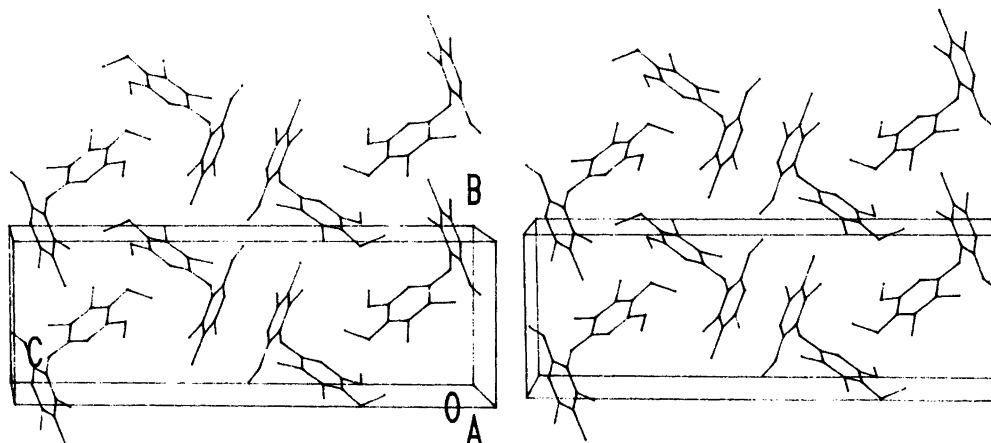
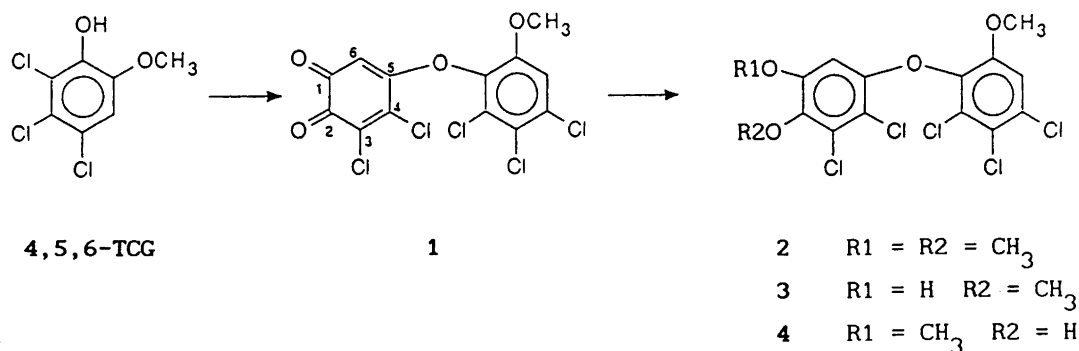


Fig. 2. Stereoscopic packing view along  $\langle 100 \rangle$ .



Scheme 1.

to which they were connected. The chlorine atoms were refined anisotropically. All other atoms were refined isotropically. The weighting scheme employed was  $w = 1/[\sigma^2(F)]$  and  $\sigma(F)$  was determined from counting statistics. In the last cycle there was no change larger than  $0.002\sigma$  in any of the 122 parameters varied. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2, bond lengths between non-hydrogen atoms in Table 3 and bond angles in Table 4. A perspective drawing of the molecule is shown in Fig. 1, and a stereoscopic drawing of the packing of 8 molecules in 2 unit cells, viewed along  $\langle 100 \rangle$  in Fig. 2. A list of observed and calculated structure factor amplitudes may be obtained upon request from one of the authors (L. Eriksson).

The aim of this study was to locate the position of the ether bridge in the molecule. Analysis indicated loss of one chlorine atom from **1**, compared with two molecules of 4,5,6-TCG. This implies that the coupling can take place in position 3,4 or 5 (see Scheme 1.) Mechanistic studies suggest that the coupling step proceeds through the initial formation of an *o*-quinone and by a nucleophilic attack of 4,5,6-TCG at the reactive site thus formed. Position 3 is, for this reason, not available for coupling and is excluded in

the present investigation. Attempts to detect more than one isomer of **2** were unsuccessful.<sup>4</sup> Since position **4** is more sterically hindered than position **5**, this may explain the apparently exclusive formation of one isomer, coupled at position **5**, as shown in this study.

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