Structure of 2,2'-Methylenebis(4-chloro-6-isopropyl-5-methylphenol)

By S. Rantsordas* and M. Perrin

Université Claude-Bernard Lyon I, Laboratoire de Minéralogie-Cristallographie Associé au CNRS (ERA 600), 43 boulevard du 11 Novembre 1918, 69622 Villeurbanne CEDEX, France

Abstract. $C_{21}H_{26}Cl_2O_2$, $M_r = 381$, m.p. $= 403$ (1) K, crystallizes in space group $P2_1/n$ with $a = 12.915$ (4), $b = 9.157$ (4), $c = 17.566$ (3) Å, $\beta = 105.22$ (3)° and $Z = 4$; $V = 2005$ (1) Å^3, $F(000) = 808$, $\mu(Cu\ K\alpha) = 3.0$ mm^{-1}; D_m (293 K, pycnometry) $= 1.29$, $D_c = 1.26$ Mg m^{-3}; $(\sin \theta/\lambda)_{max} = 0.61$ Å^{-1}. The final R value is 0.043 for 2676 reflections. The C—C—C valency angle at the methylene group is 112.1 (3)°; the dihedral angle between the two phenol rings is 107.1 (1)° and those between the isopropyl groups and the corresponding phenol rings are 93.1 (3) and 94.3 (3)°.

Introduction. As a continuation of our work (Rantsordas, Perrin & Thozet, 1978; Rantsordas, Perrin, Thozet & Lecocq, 1981), we describe now the crystal structure and molecular configuration of 2,2'-methylenebis(4-chloro-6-isopropyl-5-methylphenol) (BIPCTV) obtained by X-ray diffraction studies.

A patent for this compound presenting fungicidal and bactericidal activity was registered by Perrin, Aureille-Salvadori, Vincent-Falquet & Collange in France (1972), in Great Britain (1973), West Germany (1973) and in the USA (1979). BIPCTV was synthesized by Vincent-Falquet *et al.* (1974). By evaporation of a petroleum ether solution, transparent colourless crystals with the habit of prisms elongated along the b axis with the forms {001}, {101}, {10$\bar{1}$} and {010} were obtained.

Preliminary examination of a crystal sealed in a glass capillary using Weissenberg film methods indicated a monoclinic lattice with space group $P2_1/n$. Least-squares cell dimensions were obtained from twenty five reflections measured on the automatic diffractometer used to measure the intensities. These were collected at 293 K on an automatic Enraf–Nonius CAD-4 four-circle diffractometer by the ω–$x\theta$ scan mode over the range $1 < \theta < 70°$ using Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). From 3798 measured intensities, 2676 were considered as observed $[I > 3\sigma(I)]$ and placed on an approximately absolute scale by a Wilson (1942) plot ($B = 5.81$ Å^2). The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson,

Table 1. *Final fractional coordinates* ($\times 10^4$) *for non-hydrogen atoms, with corresponding e.s.d.'s in parentheses, and equivalent isotropic thermal parameters* (Å^2)

	x	y	z	B_{eq}^*
C(1)	4282 (3)	1856 (4)	7451 (2)	4.31
C(2)	3277 (3)	1217 (4)	7246 (2)	3.88
C(3)	2634 (3)	1434 (4)	6492 (2)	4.38
C(4)	2993 (3)	2299 (4)	5970 (2)	4.47
C(5)	4001 (3)	2943 (4)	6161 (2)	4.13
C(6)	4675 (3)	2706 (4)	6913 (2)	4.13
C(7)	5829 (3)	3305 (5)	7157 (2)	5.73
C(8)	6657 (3)	2083 (5)	7354 (3)	6.52
C(9)	6010 (4)	4426 (5)	7810 (3)	8.39
C(10)	4340 (3)	3914 (5)	5568 (2)	5.71
C(11)	3057 (2)	1444 (4)	9182 (2)	4.26
C(12)	2469 (3)	1220 (4)	8407 (2)	3.72
C(13)	1474 (3)	1890 (4)	8169 (2)	4.31
C(14)	1106 (2)	2750 (4)	8687 (2)	4.39
C(15)	1696 (2)	3023 (4)	9452 (2)	3.93
C(16)	2715 (2)	2367 (4)	9706 (2)	4.07
C(17)	3399 (3)	2631 (5)	10540 (2)	5.50
C(18)	4489 (4)	3307 (7)	10568 (3)	9.56
C(19)	3483 (4)	1235 (6)	11045 (2)	8.51
C(20)	1242 (3)	4018 (4)	9969 (2)	5.58
C(21)	2871 (3)	291 (4)	7826 (2)	4.56
Cl(4)	2115 (1)	2544 (1)	5028 (1)	6.48
Cl(14)	−178 (1)	3486 (1)	8339 (1)	6.82
O(1)	4957 (2)	1707 (3)	8193 (1)	5.58
O(11)	4044 (2)	766 (3)	9406 (1)	5.71

$$* B_{eq} = \tfrac{4}{3} \sum_i \sum_j \beta_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j.$$

1971). Atomic scattering factors for C, O and Cl were taken from *International Tables for X-ray Crystallography* (1962) and those for H from Stewart, Davidson & Simpson (1965). The refinement was made by block-diagonal least squares (Ahmed, Hall, Pippy & Huber, 1966) with the weighting scheme $\sqrt{w} = 1$ if $|F_o| < P_1$; $\sqrt{w} = P_1/|F_o|$ if $|F_o| > P_1$ with $(P_1^2/F^2)_{max} = 0.1$. The H atoms were located from a difference Fourier map and introduced in further refinement with isotropic thermal parameters of the atoms to which they are bonded, while the non-H atoms were refined with anisotropic thermal parameters. The final conventional R was 0.043. Atomic parameters with their estimated standard deviations are

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* To whom correspondence should be addressed.

Table 2. *Final fractional coordinates* $(\times 10^3)$ *for hydrogen atoms, with corresponding e.s.d.'s in parentheses, and isotropic thermal parameters* (Å^2)

	x	y	z	B
H(11)	467 (2)	119 (3)	849 (2)	5·1
H(31)	186 (2)	91 (3)	632 (2)	4·1
H(71)	590 (3)	385 (4)	670 (2)	6·4
H(81)	656 (3)	109 (4)	688 (2)	6·2
H(82)	674 (3)	166 (4)	787 (2)	6·2
H(83)	745 (3)	273 (4)	743 (2)	6·2
H(91)	553 (3)	519 (4)	763 (2)	7·9
H(92)	697 (3)	473 (4)	804 (2)	7·9
H(93)	596 (3)	420 (4)	829 (2)	7·9
H(101)	509 (2)	447 (4)	579 (2)	5·4
H(102)	378 (2)	485 (3)	539 (2)	5·4
H(103)	418 (2)	364 (3)	506 (2)	5·4
H(111)	455 (2)	78 (3)	970 (2)	5·2
H(131)	105 (2)	171 (3)	758 (2)	4·1
H(171)	302 (2)	344 (3)	1080 (2)	5·5
H(181)	486 (3)	358 (4)	1112 (2)	7·7
H(182)	447 (3)	434 (4)	1032 (2)	7·7
H(183)	493 (3)	254 (4)	1032 (2)	7·7
H(191)	397 (3)	151 (4)	1163 (2)	7·3
H(192)	405 (3)	36 (4)	1087 (2)	7·3
H(193)	270 (3)	73 (4)	1113 (2)	7·3
H(201)	180 (2)	449 (3)	1032 (2)	5·4
H(202)	100 (2)	365 (3)	1034 (2)	5·4
H(203)	85 (2)	484 (3)	967 (2)	5·4
H(211)	221 (2)	−30 (3)	748 (2)	5·0
H(212)	345 (2)	−28 (3)	813 (2)	5·0

given in Tables 1 and 2 for non-H and H atoms, respectively.*

Discussion. Fig. 1 illustrates the general view of the molecule with the numbering schemes adopted for atoms and planes. The aromatic C−C bond distances (Table 3) are normal and vary from 1·379 (5) to 1·418 (5) Å with the same mean value of 1·391 (5) for both benzene rings. The exocyclic C−C bond distances are normal: only one, C(6)−C(7) = 1·540 (5) Å, is slightly longer than the value expected for the states of hybridization involved: $C(sp^2)-C(sp^3)$ = 1·52 Å. The
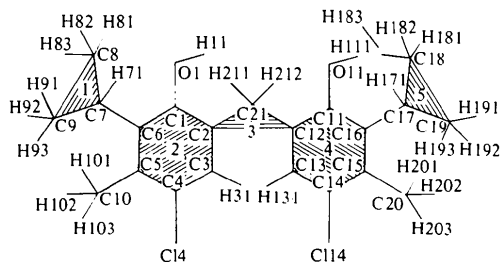
Fig. 1. Atomic and plane numbering schemes.

Table 3. *Bond distances* (Å) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·383 (5)	C(5)–C(10)	1·519 (5)	C(13)·C(14)	1·379 (5)
C(1)–C(6)	1·418 (5)	C(6) C(7)	1·540 (5)	C(14)–C(15)	1·383 (5)
C(1)–O(1)	1·370 (4)	C(7)· C(8)	1·524 (6)	C(14)–Cl(14)	1·746 (3)
C(2)–C(3)	1·381 (5)	C(7)–C(9)	1·512 (6)	C(15)–C(16)	1·408 (5)
C(2)–C(21)	1·521 (5)	C(11)· C(12)	1·389 (4)	C(15)–C(20)	1·509 (5)
C(3)–C(4)	1·381 (5)	C(11)–C(16)	1·403 (5)	C(16)–C(17)	1·518 (5)
C(4) C(5)	1·387 (5)	C(11)–O(11)	1·379 (4)	C(17) C(18)	1·526 (6)
C(4)–Cl(4)	1·757 (3)	C(12)–C(13)	1·385 (5)	C(17)–C(19)	1·544 (6)
C(5)–C(6)	1·395 (5)	C(12) C(21)	1·521 (5)		

Table 4. *Bond angles* (°) *with e.s.d.'s in parentheses*

C(2)–C(1)–C(6)	122·3 (3)	C(12)–C(11)–C(16)	123·1 (3)
C(2)–C(1)–O(1)	121·7 (3)	C(12)–C(11)–O(11)	116·1 (3)
C(6)–C(1)–O(1)	116·0 (3)	C(16)–C(11)–O(11)	120·7 (3)
C(1)–C(2)–C(3)	118·4 (3)	C(11)–C(12)–C(13)	117·2 (3)
C(1)–C(2)–C(21)	121·7 (3)	C(11)–C(12)–C(21)	122·9 (3)
C(3)–C(2)–C(21)	119·9 (3)	C(13)–C(12)–C(21)	119·9 (3)
C(2)–C(3)–C(4)	119·8 (3)	C(12)–C(13)–C(14)	120·4 (3)
C(3)–C(4)–C(5)	122·7 (3)	C(13)–C(14)–C(15)	123·2 (3)
C(3)–C(4)–Cl(4)	116·9 (3)	C(13)–C(14)–Cl(14)	116·7 (3)
C(5)–C(4)–Cl(4)	120·4 (3)	C(15)–C(14)–Cl(14)	120·1 (3)
C(4)–C(5)–C(6)	118·4 (3)	C(14)–C(15)–C(16)	117·5 (3)
C(4)–C(5)–C(10)	120·3 (3)	C(14)–C(15)–C(20)	119·5 (3)
C(6)–C(5)–C(10)	121·3 (3)	C(16)–C(15)–C(20)	123·1 (3)
C(1)–C(6)–C(5)	118·3 (3)	C(11)–C(16)–C(15)	118·6 (3)
C(1)–C(6)–C(7)	120·0 (3)	C(11)–C(16)–C(17)	121·6 (3)
C(5)–C(6)–C(7)	121·7 (3)	C(15)–C(16)–C(17)	119·8 (3)
C(6)–C(7)–C(8)	111·8 (3)	C(16)–C(17)–C(18)	113·2 (3)
C(6)–C(7)–C(9)	113·5 (3)	C(16)–C(17)–C(19)	110·9 (3)
C(8)–C(7)–C(9)	111·5 (3)	C(18)–C(17)–C(19)	113·1 (4)
		C(2)–C(21)–C(12)	112·1 (3)

C−O and C−Cl bond distances compare well with the values found in chlorophenols (Bavoux, Perrin, Thozet, Bertholon & Perrin, 1976) and in bis(chlorophenols) (Rantsordas, Perrin & Thozet, 1978; Rantsordas, Perrin, Thozet & Lecocq, 1981). The C−H bond distances vary from 0·86 (5) to 1·23 (5) Å with mean value of 1·03 (2) Å. The mean C−C−C bond angles in both benzene rings have the same value: 120·0 (8) and 120·0 (1·1)°. Only the internal angles at the substituted carbon atoms deviate from the mean value, as expected in highly substituted benzene derivatives; this could be connected with the σ-electron-withdrawing or releasing character of the substituents (Domenicano, Vaciago & Coulson, 1975). Bond angles are given in Table 4.

The dihedral angle between the two benzene rings, planes (2) and (4), is 107·1 (1)°. These planes are equally inclined with respect to plane (3), the dihedral angles they form being 100·3 (3) and 102·3 (2)°, respectively. The planes of the isopropyl groups are nearly perpendicular to the planes of the corresponding benzene rings: the dihedral angles between planes (1) and (2) and between planes (4) and (5) being respectively 94·3 (3) and 93·1 (3)°. The torsional angles involving the isopropyl group are given in Table 5. The valency angle at the methylene group C(2)−

Table 5. *Pertinent torsion angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(6)–C(7)–C(8)	61·1 (4)
C(1)–C(6)–C(7)–C(9)	–66·1 (5)
C(5)–C(6)–C(7)–C(8)	–117·2 (4)
C(5)–C(6)–C(7)–C(9)	115·6 (4)
C(11)–C(16)–C(17)–C(18)	60·3 (5)
C(11)–C(16)–C(17)–C(19)	–68·1 (4)
C(15)–C(16)–C(17)–C(18)	–121·7 (4)
C(15)–C(16)–C(17)–C(19)	110·0 (4)
C(1)–C(2)–C(21)–C(12)	79·3 (4)
C(3)–C(2)–C(21)–C(12)	–100·7 (4)
C(11)–C(12)–C(21)–C(2)	–103·0 (4)
C(13)–C(12)–C(21)–C(2)	77·0 (4)

Table 6. *Intermolecular distances* (Å) *less than* 3·6 Å *for* C–O, C–C *and* O–O *bonds and less than* 4·1 Å *for* Cl–O *and* Cl–C *bonds with e.s.d.'s in parentheses*

Symmetry code

(I)	$1 - x, 1 - y, 1 - z$	(IV)	$\frac{1}{2} - x, \frac{1}{2} + y, 1\cdot5 - z$
(II)	$1 - x, -y, 2 - z$	(V)	$-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
(III)	$\frac{1}{2} - x, -\frac{1}{2} + y, 1\cdot5 - z$		

C(10)–C(10^I)	3·553 (6)	Cl(4)– O(1^V)	3·730 (3)
C(19)–O(1^II)	3·419 (6)	Cl(14)–C(1^IV)	3·692 (4)
O(11)–O(11^II)	3·116 (4)	Cl(14)–C(2^IV)	3·829 (4)
O(11)–Cl(4^III)	3·566 (3)	Cl(14)–C(6^IV)	3·962 (4)
Cl(4)–C(11^IV)	3·859 (4)	Cl(14)–C(8^IV)	3·841 (5)
Cl(4)–C(18^V)	3·833 (5)	Cl(14)–C(19^V)	3·953 (4)
Cl(4)–C(19^IV)	3·848 (5)	Cl(14)–O(1^IV)	4·052 (3)
Cl(4)–C(20^III)	3·864 (4)		

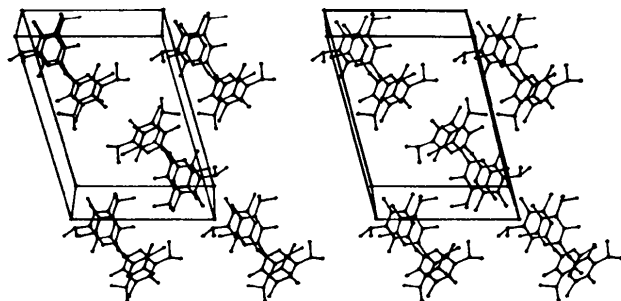
Fig. 2. A stereoscopic view of the crystal structure seen along [010].

C(21)–C(12) = 112·1 (3)° is greater than the tetrahedral angle but smaller than those found in similar compounds: 119 (6) (Whittaker, 1953), 119·2 (Chaudhuri & Hargreaves, 1956), 118·6 (4) (Rantsordas et al., 1978), 116·7 (1) (Swardstrom,

Duvall & Miller, 1972), 116 (1) and 117 (1)° (Rantsordas et al., 1981). The straight lines through C(8)–C(9) and C(18)–C(19) are inclined by 85·5 (2) and 85·0 (2)° respectively to the corresponding benzene rings.

The intermolecular distances shown in Table 6 are in the normally expected range for nonbonding contacts. A stereoscopic view of the crystal structure obtained with *ORTEP* (Johnson, 1965) is shown in Fig. 2.

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