Crystal Structure of 3,3′-Diacetyl-5,5′-dichloro-2,2′-dihydroxydiphenylmethane

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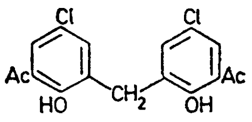
The structure of the title compound (I), has been determined by three-dimensional *X*-ray diffraction. Crystals are orthorhombic, $a = 17.22(8)$, $b = 4.25(5)$, $c = 22.04(9)$ Å, space group $Pna2_1$, with $Z = 4$. The structure was refined by least-squares based on 1 143 visually estimated intensities, to R 0.075. The dihedral angle between the two substituted phenyl rings is 117.9°.

MOSHFEGH *et al.*[1] have synthesized many compounds resembling tetracyclines in their spatial arrangement and having functional groups for chelate formation. They wished to ascertain whether or not these compounds were biologically active. For one of them, the title compound, the structure (I) was suggested. Later



(I)

Moshfegh *et al.*[2] synthesized the corresponding bromo- and fluoro-compounds. We have carried out an *X*-ray analysis to confirm the structure and to determine the spatial disposition of the two substituted phenyl rings.

EXPERIMENTAL

Crystal Data.—$C_{17}H_{14}O_4Cl_2$, $M = 353.2$. Orthorhombic, $a = 17.22(8)$, $b = 4.25(5)$, $c = 22.04(9)$ Å, $U = 1\,613.2$ Å^3, $D_m = 1.47$ g cm^{-3}, $Z = 4$, $D_c = 1.45$ g cm^{-3}, $F(000) = 728$. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 37.7 cm^{-1}.

Weissenberg photographs showed the systematic absences to be: $0kl$, $k + l = 2n + 1$ and $h0l$, $h = 2n + 1$ consistent with space groups $Pna2_1$, or $Pnam$; the former was shown to be correct from the subsequent solution and refinement of the structure.

A crystal of dimensions *ca.* 0.2 × 0.2 × 0.5 mm^3 was used for the collection of intensity data. Multiple-film Weissenberg photographs were taken with Cu-K_α radiation for layers $h0$—$3l$ for oscillation of the crystal around the b axis. The intensities of 1 143 independent reflections were measured visually, and Lorentz and polarization factors applied.

Structure Determination and Refinement.—N.R.C. crystallographic programs [3] were for the solution and refinement of the structure. Calculations were carried out on an IBM 370/135 computer at Pahlavi University.

The two independent chlorine atom positions were derived from a three-dimensional Patterson map. These positions were refined, and their contributions to the

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[1] A. A. Moshfegh, S. Fallab, and H. Erlenmeyer, *Helv. Chim. Acta*, 1957, **40**, 1157.

[2] A. A. Moshfegh and B. Rozzpeikar, 1971, and A. A. Moshfegh and R. Badri, 1973, M.Sc. Theses, Pahlavi University.

[3] F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, 1966, N.R.C. Crystallographic Programs for the IBM 360 System, World list of Crystallographic Computer Programs, 2nd edn., Appendix, Oesthock, Utrecht, p. 52. These programs were adapted for an IBM 370 135 computer.

structure factors were calculated. Only the terms $|F_{\mathrm{Cl}}| \geqslant |F_{\mathrm{o}}|/2$ were used for the first partial three-dimensional Fourier map, which showed 8 possible peaks. The remaining atoms emerged from the next three Fourier maps. Scattering factors for non-hydrogen atoms were taken from ref. 4, and for hydrogen atoms from ref. 5, with chlorine corrections for anomalous dispersion ($\Delta f'$ and $\Delta f''$) taken from ref. 6.

Five cycles of block-diagonal isotropic least-squares refinement reduced R to 0.16 and four further cycles of anisotropic least-squares to 0.095. An agreement analysis was then run on the data, and layers scaled accordingly. A difference-Fourier map at this stage revealed all 14 hydrogen-atom positions. In the next 3 cycles of refinement hydrogen atoms were allowed for as fixed-atom contributions with isotropic temperature factors 0.5 Å^2 higher than those at their parent atoms; R fell to 0.075. Refinement of hydrogen atoms was attempted but led to some unacceptable bond lengths, angles, and temperature factors and no improvement in R. Evidently the accuracy of the data did not justify such refinement. A weighting scheme[7] of the form $\sqrt{w} = 1$ for $|F_{\mathrm{o}}| \leqslant P$ and $\sqrt{w} = P/|F_{\mathrm{o}}|$ if $|F_{\mathrm{o}}| > P$ where $P = 12$ was used throughout refinement.

RESULTS AND DISCUSSION

Final co-ordinates for non-hydrogen atoms with their standard deviations are listed in Table 1, and for hydrogen atoms in Table 2. Anisotropic temperature factors and observed and calculated structure factors are listed in Supplementary Publication No. SUP 21578 (5 pp.).* Bond lengths, valence angles, and intermolecular contacts are listed in Tables 3—5, and details of least-square planes in Table 6.

Figure 1 depicts one molecule and shows the atom numbering scheme used. Figure 2 shows the [010] projection of the structure.

TABLE 1

Fractional co-ordinates ($\times 10^4$) for the non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x	y	z
Cl	6 238(1)	4 795(8)	0
C(1)	3 980(5)	3 177(19)	375(3)
C(2)	3 616(4)	4 842(18)	−110(3)
C(3)	4 049(4)	6 354(19)	−573(3)
C(4)	4 877(4)	6 274(18)	−530(4)
C(5)	5 224(4)	4 776(21)	−45(4)
C(6)	4 783(5)	3 242(20)	400(4)
C(7)	3 657(5)	7 925(21)	−1 087(4)
C(8)	4 120(6)	9 156(26)	−1 611(4)
C(9)	3 496(5)	1 481(20)	835(4)
O(10)	2 823(3)	4 823(15)	−118(3)
O(11)	2 942(4)	8 116(21)	−1 099(4)
Cl′	1 118(1)	7 681(8)	1 744(1)
C(1′)	3 152(4)	3 485(19)	1 339(3)
C(2′)	3 611(4)	4 346(19)	1 850(3)
C(3′)	3 308(4)	6 137(18)	2 321(3)
C(4′)	2 533(5)	7 164(21)	2 288(3)
C(5′)	2 089(4)	6 326(21)	1 787(4)
C(6′)	2 384(5)	4 582(22)	1 318(3)
C(7′)	3 782(5)	6 902(23)	2 867(4)
C(8′)	3 444(7)	8 690(29)	3 397(5)
O(10′)	4 349(3)	3 205(17)	1 849(3)
O(11′)	4 469(4)	5 890(22)	2 891(3)

TABLE 2

Fractional co-ordinates ($\times 10^3$) for hydrogen atoms (derived from $\Delta\rho$ map and unrefined)

Atom	Attached to	x	y	z
H(4)	C(4)	513	790	−77
H(6)	C(6)	509	175	76
H(81)	C(8)	394	58	−197
H(82)	C(8)	451	775	−174
H(83)	C(8)	440	91	−132
H(91)	C(9)	313	23	69
H(92)	C(9)	390	−54	107
H(10)	O(10)	282	496	−64
H(4′)	C(4′)	237	834	263
H(6′)	C(6′)	216	438	99
H(81′)	C(8′)	374	9	366
H(82′)	C(8′)	321	5	306
H(83′)	C(8′)	296	732	363
H(10′)	O(10′)	443	377	216

TABLE 3

Bond lengths (Å), with estimated standard deviations in parentheses

Cl–C(5)	1.748(7)	Cl′–C(5′)	1.772(8)
C(1)–C(2)	1.43(1)	C(1′)–C(2′)	1.42(1)
C(1)–C(6)	1.38(1)	C(1′)–C(6′)	1.40(1)
C(1)–C(9)	1.50(1)	C(1′)–C(9)	1.52(1)
C(2)–C(3)	1.42(1)	C(2′)–C(3′)	1.39(1)
C(2)–O(10)	1.37(1)	C(2′)–O(10′)	1.36(1)
C(3)–C(4)	1.43(1)	C(3′)–C(4′)	1.41(1)
C(3)–C(7)	1.48(1)	C(3′)–C(7′)	1.49(1)
C(4)–C(5)	1.38(1)	C(4′)–C(5′)	1.39(1)
C(5)–C(6)	1.40(1)	C(5′)–C(6′)	1.37(1)
C(7)–C(8)	1.50(1)	C(7′)–C(8′)	1.51(1)
C(7)–O(11)	1.23(1)	C(7′)–O(11′)	1.26(1)
O(10) $\cdots$ O(11)	2.59(1)	O(10′) $\cdots$ O(11′)	2.57(1)

TABLE 4

Valence angles (°), with estimated standard deviations in parentheses

C(2)–C(1)–C(6)	117.3(7)	C(2′)–C(1′)–C(6′)	117.6(7)
C(2)–C(1)–C(9)	120.2(7)	C(2′)–C(1′)–C(9)	120.5(7)
C(6)–C(1)–C(9)	122.6(7)	C(6′)–C(1′)–C(9)	122.0(7)
C(1)–C(2)–C(3)	122.3(7)	C(1′)–C(2′)–C(3′)	121.7(7)
C(1)–C(2)–O(10)	116.5(6)	C(1′)–C(2′)–O(10′)	115.1(7)
C(3)–C(2)–O(10)	121.3(7)	C(3′)–C(2′)–O(10′)	123.2(7)
C(2)–C(3)–C(4)	117.8(7)	C(2′)–C(3′)–C(4′)	119.2(7)
C(2)–C(3)–C(7)	121.1(7)	C(2′)–C(3′)–C(7′)	121.2(7)
C(4)–C(3)–C(7)	121.1(6)	C(4′)–C(3′)–C(7′)	119.6(7)
C(3)–C(4)–C(5)	119.6(7)	C(3′)–C(4′)–C(5′)	119.0(7)
C(4)–C(5)–C(6)	121.4(8)	C(4′)–C(5′)–C(6′)	122.3(8)
C(4)–C(5)–Cl	118.3(6)	C(4′)–C(5′)–Cl′	118.6(6)
C(6)–C(5)–Cl	120.3(6)	C(6′)–C(5′)–Cl′	119.1(6)
C(5)–C(6)–C(1)	121.6(7)	C(5′)–C(6′)–C(1′)	120.3(7)
C(3)–C(7)–C(8)	120.4(7)	C(3′)–C(7′)–C(8′)	121.6(8)
C(3)–C(7)–O(11)	120.0(8)	C(3′)–C(7′)–O(11′)	118.3(8)
C(8)–C(7)–O(11)	119.5(8)	C(8′)–C(7′)–O(11′)	120.0(8)
C(1)–C(9)–C(1′)	116.1(7)		

TABLE 5

Intermolecular contacts $\leqslant$3.6 Å involving non-hydrogen atoms

Cl $\cdots$ O(10$^{\mathrm{I}}$)	3.38	O(10) $\cdots$ O(11$^{\mathrm{VII}}$)	3.59
C(1) $\cdots$ C(3$^{\mathrm{II}}$)	3.58	O(11) $\cdots$ C(8$'^{\mathrm{VIII}}$)	3.55
C(2) $\cdots$ C(9$^{\mathrm{III}}$)	3.52	O(11) $\cdots$ C(8$'^{\mathrm{IX}}$)	3.24
C(8) $\cdots$ O(11$'^{\mathrm{IV}}$)	3.43	Cl′ $\cdots$ O(10$'^{\mathrm{X}}$)	3.52
C(8) $\cdots$ O(11$'^{\mathrm{V}}$)	3.40	C(1′) $\cdots$ C(4$'^{\mathrm{XI}}$)	3.57
O(10) $\cdots$ (Cl$^{\mathrm{VI}}$)	3.57		

* Roman numeral superscripts denote the following equivalent positions, relative to the reference molecule at x,y,z:

I $\frac{1}{2} + x, \frac{1}{2} - y, z$
II $x, y - 1, z$
III $x, 1 + y, z$
IV $1 - x, 1 - y, z - \frac{1}{2}$
V $1 - x, 2 - y, z - \frac{1}{2}$
VI $\frac{1}{2} + x, 1\frac{1}{2} - y, z$
VII $x, y - 1, z$
VIII $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$
IX $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$
X $x - \frac{1}{2}, 1\frac{1}{2} - y, z$
XI $x, y - 1, z$

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

Bond lengths and valence angles are almost all as expected, and match closely in the two substituted phenyl rings. The mean C–C lengths in the two phenyl rings (1.40 and 1.41 Å) are close to the accepted value [1.395(3) Å].[8] The mean C–C bond length adjacent to the carbonyl group (1.505 Å) is not significantly shorter than that (1.516 Å) quoted in ref. 8. The two C(ring)–C(carbonyl) bonds (1.48 and 1.49 Å) are not significantly different from those (1.489—1.512 Å) reported for hemimellitic acid,[9] and the standard $C(sp^2)$–$C(sp^2)$ single-bond length (1.474 Å).[10] The mean of the two $C(sp^3)$–$C(sp^2)$ bonds (1.51 Å) is as expected.

TABLE 6

Equations of planes in the form: $lX + mY + nZ - P = 0$, where X,Y,Z are absolute co-ordinates (in Å), l, m, and n are the direction cosines of the normal to the plane, and P is the distance of the plane from the origin. Deviations of the atoms (Å × 10^3), with estimated standard deviations in parentheses, are given in square brackets

Plane (*A*): Cl, C(1)—(9), O(10), O(11)

$0.0209X - 0.8512Y - 0.5244Z + 1.4706 = 0$

[Cl −43(3), C(1) 28(8), C(2) −28(8), C(3) −26(8), C(4) −16(8), C(5) −21(9), C(6) 4(8), C(7) −15(9), C(8) 160(11), C(9) 94(8), O(10) −40(6), O(11) −96(9)]

Plane (*B*): C(9), Cl′, C(1′)—(8′), O(10′), O(11′)

$0.3077X + 0.8366Y - 0.4532Z - 1.5852 = 0$

[C(9) −38(8), Cl′ 2(3), C(1′) −10(8), C(2′) 29(8), C(3′) 36(8), C(4′) 25(9), C(5′) −8(9), C(6′) −5(9), C(7′) 15(10), C(8′) −55(12), O(10′) 14(7), O(11′) −5(9)]

Plane (*C*): C(1)—(6)

$0.0218X - 0.8431Y - 0.5374Z + 1.4550 = 0$

[C(1) 18(8), C(2) −18(8), C(3) 2(8), C(4) 12(8), C(5) −11(9), C(6) −4(8)]

Plane (*D*): C(1′)—(6′)

$0.2968X + 0.8325Y - 0.4678Z - 1.4753 = 0$

[C(1′) −8(8), C(2′) 4(8), C(3′) 0(8), C(4′) 1(9), C(5′) −6(9), C(6′) 9(9)]

Plane (*E*): Cl, C(7), C(9), O(10)

$0.0290X - 0.8398Y - 0.5421Z + 1.3885 = 0$

[Cl −15(3), C(7) 34(9), C(9) 35(8), O(10) −55(6)]

Plane (*F*): C(9), Cl′, C(7′), O(10′)

$0.3064X + 0.8320Y - 0.4625Z - 1.5296 = 0$

[C(9) −10(8), Cl′ 4(3), C(7′) −10(10), O(10′) 16(7)]

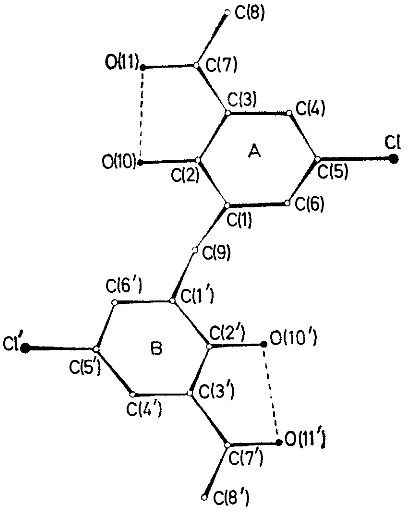

FIGURE 1 The structure of (I)

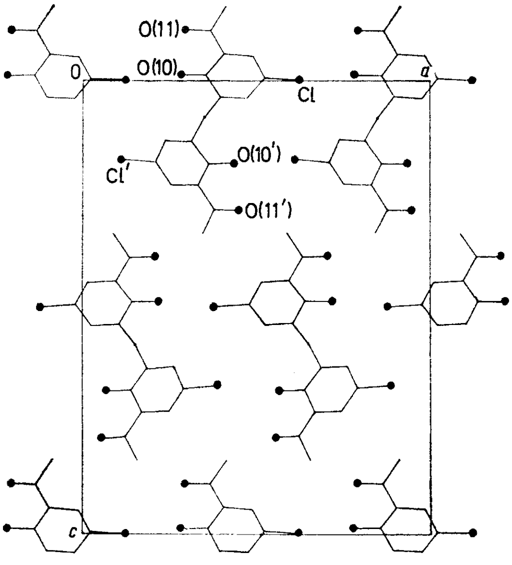

FIGURE 2 [010] Projection of (I)

The mean of two C–O single bonds (1.365 Å) compares well with the 1.36 Å (ref. 8) for a shortened single bond in the presence of an aromatic ring. One C=O bond length (1.23 Å) is as expected,[8] but the other (1.26 Å) is significantly longer.

The mean Cl–C distance (1.760 Å) agrees well with the sum of the covalent radii (1.762 Å),[11] but is slightly longer than those in *p*-chloro-*trans*-cinnamic acid (0.741 Å) and β-(*p*-chlorophenyl)propionic acid (1.797 Å).[12]

The internal angles in the phenyl rings deviate from the expected 120° only at the substituted carbon atoms, as expected for highly substituted benzene derivatives.[13] No atoms in the rings deviate from the least-squares plane through them by <0.02 (ring A) or 0.01 Å (ring B). The dihedral angle between the rings is 117.9°.

There are two short intermolecular contacts: O(10)–H ⋯ O(11) 2.59 and O(10′)–H ⋯ O(11′) 2.57 Å; these are clearly strong hydrogen bonds. The only intermolecular contacts $\leqslant 3.6$ Å are given in Table 5. The four intermolecular contacts $\leqslant 3.5$ Å [Cl ⋯ O(10) 3.38,

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C(8) · · · O(11′) 3.40, 3.43, and O(11) · · · C(8′) 3.24 Å] are not especially short and are normal van der Waals contacts.

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