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3,5-Dichloro-2,6-dimethoxycyclohexa-2,5-diene-1,4-dione

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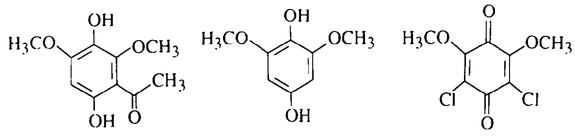
Abstract

A new synthesis of the title compound, $C_8H_6Cl_2O_4$, is described. The molecule has a mirror plane and the six-membered carbon ring assumes a slight boat conformation. The ring substituents are arranged in an alternating 'up and down' pattern with respect to the best plane through the ring C atoms.

Comment

Dichlorodimethoxycyclohexadiene-1,4-diones are reported to possess bacteriostatic activity against gram positive bacteria (Hayashi, 1954) and they are also good synthons in different types of Diels–Alder (Mehta, Srikrishna, Veera Reddy & Nair, 1981) and 1,3-dipolar cycloaddition reactions (Shiraishi, Ikeuchi, Seno & Asahara, 1978). The preparation of a useful synthon, 3,6-dihydroxy-2,4-dimethoxyacetophenone, (I), for the preparation of a range of chalcones and other flavonoids, was attempted *via* the acylation of 1,4-dihydroxy-2,6-dimethoxybenzene, (II), using the Hoesch reaction (Norman, 1978). The reaction failed to produce compound (I), but instead gave 3,5-dichloro-2,6-dimethoxycyclohexa-2,5-diene-1,4-dione, (III). Compound (III) has been synthesized previously by two different methods (Lindberg, 1953; Davidge, Davies, Kenyon & Mason, 1958), but its spectral and structural characteristics have not been reported. We obtained (III) in the form of bright orange crystals. The X-ray structure and other spectral data reported here were determined in order to assign its constitution unambiguously.



(I) (II) (III)

The molecular structure of (III) is represented in Fig. 1. The ring is bisected by a mirror plane passing through O1, C1, C4 and O3. The C1—O1 and C4—O3 bond lengths are the same within experimental error, and are consistent with double bonding. The C2—C3 bond length of 1.340 (2) Å is also indicative of double bonding. All of the bond lengths and angles are unexceptional.

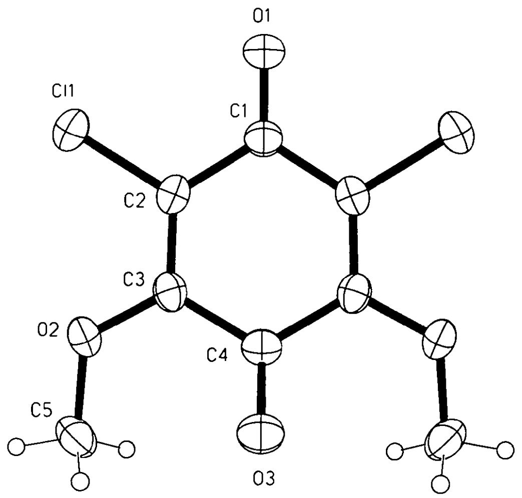


Fig. 1. View of the molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

The six-membered carbon ring has a slight boat conformation; this contrasts with that of unsubstituted 2,5-cyclohexadiene-1,4-dione which has a chair conformation (van Bolhuis & Kiers, 1978). Deviations from the best least-squares plane through the six C atoms in the ring are: C1 0.063 (2), C2, C2*a* −0.021 (1), C3, C3*a*

−0.061 (1) and C4 0.101 (2) Å. An alternative view of this lack of planarity is indicated by the dihedral angle of 11.21 (12)° between the least-squares planes through the ring atoms on each side of the mirror plane.

The peripheral atoms or groups attached to the ring C atoms display a pattern of alternating 'up and down' deviations from the best plane through the ring. The largest deviation of 0.436 (3) Å occurs for O3, with the adjacent methoxy O atoms projecting −0.098 (2) Å in the opposite direction. A smaller deviation of 0.166 (3) Å is observed for O1 with the adjacent Cl atoms at −0.053 (2) Å. This feature can be ascribed to steric interactions between the substituents.

Experimental

1,4-Dihydroxy-2,6-dimethoxybenzene [(II), 4 g, 0.0235 mol, prepared by the method of Baker (1941)] was dissolved in dry diethyl ether (200 ml); acetonitrile (1.2 ml, 0.0235 mol) and fused zinc chloride (5 g) were added. Dry HCl gas was passed through the reaction mixture for 4 h at 273 K. The reaction mixture was kept in an ice chest for 12 h. When an oily layer separated out, water (200 ml) was added and the mixture boiled for 2 h. The brown precipitate was filtered and compound (III) obtained from the residue by column chromatography over silica gel [(III) eluted out from ethyl acetate–petroleum ether, 3:17]; it crystallized out from chloroform as fine bright-orange crystals (800 mg), m.p. 428–429 K. IR (KBr) ν_{max}: 3000, 1685 (C=O), 1660, 1650, 1630, 1580, 1460, 1300, 1160, 1080, 975, 910 and 810 cm^{-1}. UV ($CHCl_3$) λ_{max} (log ε): 301 (2.28) and 409 (*br*, 0.044) nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.18 (*s*, C-3 OCH_3 and C-5 OCH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 61.7 (C-3 OCH_3 and C-5 OCH_3), 124.7 (C-3 and C-5), 153.1 (C-2 and C-6), 173.8 (C-4) and 175.8 (C-1).

Crystal data

$C_8H_6Cl_2O_4$
$M_r = 237.03$
Orthorhombic
Pnma
$a = 9.840 (7)$ Å
$b = 16.198 (12)$ Å
$c = 5.690 (4)$ Å
$V = 906.9 (11)$ Å^3
$Z = 4$
$D_x = 1.736$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 27 reflections
$\theta = 9–12°$
$\mu = 0.698$ mm^{-1}
$T = 210 (2)$ K
Irregular block
0.71 × 0.53 × 0.46 mm
Orange

Data collection

Siemens *P3R3* diffractometer
$\omega–2\theta$ scans
Absorption correction: none
897 measured reflections
836 independent reflections
780 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0158$
$\theta_{max} = 25.04°$
$h = 0 \rightarrow 11$
$k = -1 \rightarrow 19$
$l = 0 \rightarrow 6$
3 standard reflections monitored every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0342$
$wR(F^2) = 0.0895$
$S = 1.070$
836 reflections
72 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.2335P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.350$ e Å^{-3}
$\Delta\rho_{min} = -0.314$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.1215 (77)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl1	0.77934 (5)	0.41765 (3)	0.22049 (9)	0.0370 (3)
O1	0.8619 (2)	1/4	0.0886 (3)	0.0380 (5)
O2	0.60524 (13)	0.40178 (7)	0.6233 (2)	0.0383 (4)
O3	0.5719 (2)	1/4	0.8630 (3)	0.0399 (5)
C1	0.7813 (2)	1/4	0.2507 (4)	0.0270 (6)
C2	0.7284 (2)	0.32727 (10)	0.3518 (3)	0.0265 (4)
C3	0.6453 (2)	0.32901 (9)	0.5384 (3)	0.0264 (4)
C4	0.6136 (2)	1/4	0.6631 (4)	0.0263 (5)
C5	0.4890 (2)	0.40990 (13)	0.7762 (3)	0.0377 (5)

Table 2. *Selected geometric parameters (Å, °)*

Cl1—C2	1.718 (2)	C1—C2	1.472 (2)
O1—C1	1.217 (3)	C1—C2^i	1.472 (2)
O2—C3	1.334 (2)	C2—C3	1.340 (2)
O2—C5	1.443 (2)	C3—C4	1.497 (2)
O3—C4	1.209 (3)	C4—C3^i	1.497 (2)
C3—O2—C5	122.24 (13)	O2—C3—C2	119.09 (14)
O1—C1—C2	121.76 (10)	O2—C3—C4	121.48 (15)
C2—C1—C2^i	116.5 (2)	C2—C3—C4	119.02 (15)
C3—C2—C1	122.87 (15)	O3—C4—C3	121.13 (10)
C3—C2—Cl1	120.28 (13)	C3^i—C4—C3	117.6 (2)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

The temperature of the crystal was controlled using an Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986). H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; each H atom was given an isotropic displacement parameter equal to 1.5 times the equivalent isotropic displacement parameter of the atom to which it is attached.

Data collection: Siemens *P3R3* system. Cell refinement: Siemens *P3R3* system. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93.

We acknowledge the use of the EPSRC Chemical Database Service at Daresbury Laboratory for access to the Cambridge Structural Database (Allen *et al.*, 1991).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1054). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,5-Anhydro-2,3-dideoxy-2-(guanin-9-yl)-D-*arabino*-hexitol

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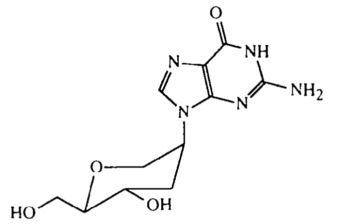
Abstract

The molecular shape of the title compound, $C_{11}H_{15}N_5O_4$, in the crystalline state is characterized by the chair conformation of the sugar moiety and the axial position of the guanine substituent.

Comment

Interest in pyranose nucleosides has grown recently because of the discovery of the interesting antiviral activity of anhydrohexitol nucleosides (Verheggen *et al.*, 1993) and because of their use as building blocks for oligonucleotides (Eschenmoser, 1993; Herdewijn *et al.*, 1994). Oligonucleotides composed of 1,5-anhydrohexitol nucleosides were shown to hybridize strongly with natural DNA and RNA and to be enzymatically stable (Van Aerschot, Verheggen, Hendrix & Herdewijn, 1995). In order to verify the influence of the incorporation of the six-membered anhydrohexitol ring on the nucleoside and oligonucleotide conformation, single-crystal structure determinations of these building units were undertaken. The structure of the title compound, (I), is reported here.



(I)

The title compound was synthesized as described previously (Verheggen *et al.*, 1993) and crystallized in the orthorhombic space group $P2_12_12_1$, containing one molecule in the asymmetric unit. The molecular structure with the labelling scheme is shown in Fig. 1.

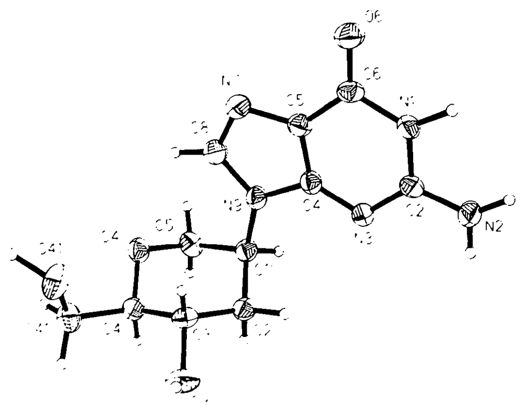


Fig. 1. View of the molecule with atomic labelling, showing 50% probability displacement ellipsoids (*SHELXTL/PC*: Sheldrick 1990). H atoms are shown as small circles of arbitrary radii.

The heterocyclic base points away from the sugar moiety (*anti* orientation), as reflected by the glycosidic torsion angle χ, C5′—C1′—N9—C4 = −167.7 (3)°, which is in the usual range for purine nucleosides (Saenger, 1984). Bond lengths and angles of the base are in the normal range for guanine derivatives (Taylor & Kennard, 1982). The best plane through the guanine ring (r.m.s. deviation 0.024 Å) makes an angle of 82.1 (1)° with the best plane through the anhydrohexitol ring (r.m.s. deviation 0.231 Å).