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5'-(2-Hydroxy-5-hydroxymethyl-3-methoxyphenyl)-6,9-bis(hydroxymethyl)-3',4,11-trimethoxydibenzo[d,f][1,3]dioxepine-2-spiro-4'-cyclohexa-2',5'-dienone

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Abstract

The title compound $C_{31}H_{30}O_{11}$, an oxidation product of dehydrodivanillyl alcohol, contains two *o,o*-dihydroxybiphenyl ring systems joined together with a dioxepin ring structure.

Comment

During our exploration of the oxidative coupling behaviour of *o,o*-dihydroxybiphenyl compounds related to

wood lignins, we have obtained a tetrameric dibenzo[d,f][1,3]dioxepin, (I), from dehydrodivanillyl alcohol as bright yellow crystals. The reaction involves a side-chain elimination, a reaction that has been observed previously during dehydrogenation of lignin model compounds with *p*-hydroxybenzyl alcohol structures (Pew & Connors, 1969).

(I)
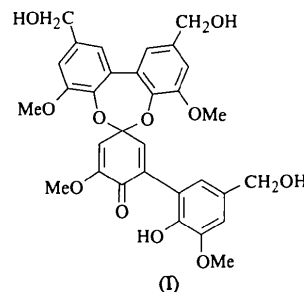
The geometry and numbering scheme of the molecule are shown in Fig. 1. The aromatic ring with a free phenolic group was found to be at an expected angle of 56.4 (1)° to the cyclohexadione ring and a hydrogen-bonding interaction can be observed between the phenolic OH (O5) and the cyclohexadienone carbonyl oxygen O4. The benzene rings in the dioxepin moiety are at an angle of 41.7 (1)°, which is considerably less than in normal biphenyl structures (57–59°).

The molecules are held together by hydrogen bonds between the terminal OH groups. The hydrogen-bonding details are given in Table 3.
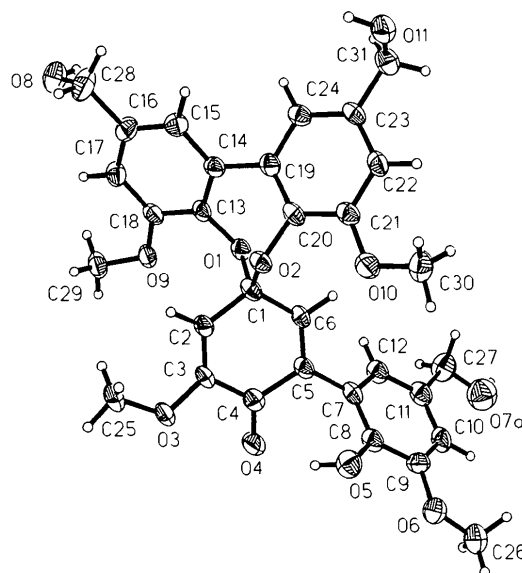

Fig. 1. Molecular geometry and the numbering scheme for the title compound. Displacement ellipsoids are plotted at the 30% probability level. Only one orientation of the disordered hydroxyl group is shown.

$C_{31}H_{30}O_{11}$

Experimental

The title compound was obtained by oxidative coupling of dehydrodivanillyl alcohol. The oxidants were hydrogen peroxide catalyzed by horseradish peroxidase in a mixture of dioxane and an aqueous buffer at pH 6, or silver oxide. The product was isolated from the reaction mixture using column chromatography (Karhunen, Rummakko, Pajunen & Brunow, 1996). Crystals of the title compound were obtained from a mixture of ethyl acetate and acetone at room temperature.

Crystal data

$C_{31}H_{30}O_{11}$	Mo $K\alpha$ radiation
$M_r = 578.55$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25
$Pbca$	reflections
$a = 22.934\,(5)$ Å	$\theta = 7.12-10.67°$
$b = 21.728\,(4)$ Å	$\mu = 0.105$ mm^{-1}
$c = 11.217\,(2)$ Å	$T = 193\,(2)$ K
$V = 5589.5\,(19)$ Å^3	Prism
$Z = 8$	$0.40 \times 0.35 \times 0.20$ mm
$D_x = 1.375$ Mg m^{-3}	Yellow
$D_m = 1.37\,(2)$ Mg m^{-3}	
D_m measured by flotation	

Data collection

Rigaku AFC-7S diffractom-	$\theta_{max} = 24.99°$
eter	$h = 0 \rightarrow 27$
$2\theta/\omega$ scans	$k = 0 \rightarrow 25$
Absorption correction:	$l = 0 \rightarrow 13$
none	3 standard reflections
4911 measured reflections	monitored every 200
4911 independent reflections	reflections
2522 observed reflections	intensity decay: none
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.005$
$R[F^2 > 2\sigma(F^2)] = 0.0547$	$\Delta\rho_{max} = 0.325$ e Å^{-3}
$wR(F^2) = 0.1379$	$\Delta\rho_{min} = -0.323$ e Å^{-3}
$S = 0.861$	Extinction correction: none
4911 reflections	Atomic scattering factors
379 parameters	from *International Tables*
H-atom parameters not	*for Crystallography* (1992,
refined	Vol. C, Tables 4.2.6.8 and
$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2]$	6.1.1.4)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

	x	y	z	U_{eq}
O1	0.28309 (8)	0.81416 (9)	0.2445 (2)	0.0455 (5)
O2	0.27306 (8)	0.91301 (9)	0.3262 (2)	0.0467 (5)
O3	0.41186 (9)	0.81450 (11)	0.5557 (2)	0.0628 (6)
O4	0.48517 (10)	0.83494 (12)	0.3821 (2)	0.0769 (8)
O5	0.50197 (10)	0.96652 (11)	0.3178 (2)	0.0725 (7)
O6	0.58564 (11)	1.00363 (12)	0.1782 (2)	0.0733 (7)
O7A†	0.5535 (4)	0.8912 (5)	−0.2137 (8)	0.116 (4)
O7B‡	0.5685 (3)	0.8589 (4)	−0.1829 (6)	0.098 (3)
O8	0.05497 (11)	0.67768 (12)	0.4238 (2)	0.0815 (8)
O9	0.27541 (9)	0.70773 (10)	0.3641 (2)	0.0583 (6)
O10	0.29329 (10)	1.01738 (10)	0.2031 (2)	0.0663 (6)
O11	0.07277 (11)	1.02570 (12)	0.0179 (2)	0.0754 (7)
C1	0.31305 (13)	0.86274 (14)	0.3068 (2)	0.0458 (8)
C2	0.33265 (14)	0.84226 (13)	0.4268 (2)	0.0473 (8)
C3	0.38856 (14)	0.83441 (14)	0.4526 (2)	0.0480 (8)
C4	0.4342 (2)	0.8474 (2)	0.3631 (3)	0.0558 (9)
C5	0.41692 (14)	0.87872 (14)	0.2499 (2)	0.0479 (8)
C6	0.35997 (13)	0.88300 (14)	0.2259 (2)	0.0466 (8)
C7	0.46319 (14)	0.89979 (14)	0.1683 (2)	0.0490 (8)
C8	0.50438 (14)	0.9420 (2)	0.2068 (3)	0.0535 (8)
C9	0.54797 (14)	0.9616 (2)	0.1280 (3)	0.0595 (9)
C10	0.5508 (2)	0.9384 (2)	0.0135 (3)	0.0630 (10)
C11	0.5091 (2)	0.8956 (2)	−0.0256 (3)	0.0616 (9)
C12	0.46655 (15)	0.8760 (2)	0.0521 (3)	0.0594 (9)
C13	0.22954 (13)	0.79643 (14)	0.2928 (2)	0.0438 (7)
C14	0.18094 (13)	0.83256 (15)	0.2721 (2)	0.0481 (8)
C15	0.12685 (14)	0.8127 (2)	0.3127 (3)	0.0569 (9)
C16	0.12163 (14)	0.7592 (2)	0.3758 (3)	0.0662 (10)
C17	0.17091 (14)	0.7221 (2)	0.3946 (3)	0.0585 (9)
C18	0.22476 (13)	0.7406 (2)	0.3525 (3)	0.0512 (8)
C19	0.18858 (13)	0.89113 (14)	0.2058 (2)	0.0479 (8)
C20	0.23708 (13)	0.92899 (14)	0.2307 (2)	0.0481 (8)
C21	0.24518 (14)	0.98425 (15)	0.1694 (3)	0.0528 (8)
C22	0.20572 (14)	1.0006 (2)	0.0831 (3)	0.0547 (8)
C23	0.15668 (14)	0.9650 (2)	0.0578 (3)	0.0516 (8)
C24	0.14837 (13)	0.91009 (14)	0.1201 (2)	0.0489 (8)
C25	0.3723 (2)	0.8022 (2)	0.6502 (3)	0.0797 (12)
C26	0.6343 (2)	1.0198 (2)	0.1107 (3)	0.0937 (14)
C27	0.5078 (2)	0.8693 (2)	−0.1516 (3)	0.0860 (13)
C28	0.0629 (2)	0.7404 (2)	0.4258 (4)	0.0940 (14)
C29	0.2742 (2)	0.6576 (2)	0.4437 (3)	0.0714 (11)
C30	0.2977 (2)	1.0792 (2)	0.1597 (3)	0.0766 (11)
C31	0.1151 (2)	0.9847 (2)	−0.0356 (3)	0.0650 (10)

† Site occupancy = 0.48 (2).   ‡ Site occupancy = 0.52 (2).

Table 2. Selected geometric parameters (Å, °)

O1—C13	1.397 (3)	O10—C21	1.370 (4)
O1—C1	1.441 (3)	O10—C30	1.433 (4)
O2—C20	1.396 (3)	O11—C31	1.448 (4)
O2—C1	1.443 (3)	C1—C6	1.475 (4)
O3—C3	1.346 (3)	C1—C2	1.487 (4)
O3—C25	1.420 (4)	C2—C3	1.326 (4)
O4—C4	1.218 (4)	C3—C4	1.478 (4)
O5—C8	1.355 (3)	C4—C5	1.494 (4)
O6—C9	1.377 (4)	C5—C6	1.337 (4)
O6—C26	1.393 (4)	C5—C7	1.475 (4)
O7A—C27	1.345 (8)	C11—C27	1.524 (5)
O7B—C27	1.453 (8)	C14—C19	1.484 (4)
O8—C28	1.375 (4)	C16—C28	1.514 (5)
O9—C18	1.370 (4)	C23—C31	1.480 (4)
O9—C29	1.409 (3)		
C13—O1—C1	115.6 (2)	O5—C8—C9	119.3 (3)
C20—O2—C1	116.6 (2)	O6—C9—C10	126.4 (3)
C3—O3—C25	116.6 (2)	O6—C9—C8	113.0 (3)
C9—O6—C26	116.6 (3)	C10—C9—C8	120.6 (3)
C18—O9—C29	116.5 (2)	C12—C11—C27	117.2 (3)
C21—O10—C30	117.1 (3)	C10—C11—C27	123.5 (3)
O1—C1—O2	108.9 (2)	C14—C13—O1	119.1 (3)
O1—C1—C6	105.5 (2)	C18—C13—O1	119.8 (3)
O2—C1—C6	109.3 (2)	C13—C14—C19	118.4 (3)
O1—C1—C2	111.4 (2)	C15—C14—C19	122.4 (3)
O2—C1—C2	106.4 (2)	C15—C16—C28	119.9 (3)
C6—C1—C2	115.2 (3)	C17—C16—C28	120.4 (3)
C3—C2—C1	121.9 (3)	O9—C18—C17	125.0 (3)
C2—C3—O3	127.8 (3)	O9—C18—C13	115.7 (3)
C2—C3—C4	120.8 (3)	C24—C19—C14	121.4 (3)
O3—C3—C4	111.4 (3)	C20—C19—C14	119.6 (3)
O4—C4—C3	121.2 (3)	C21—C20—O2	120.9 (3)
O4—C4—C5	120.3 (3)	O2—C20—C19	118.2 (3)
C3—C4—C5	118.4 (3)	O10—C21—C22	126.1 (3)
C6—C5—C7	123.8 (3)	O10—C21—C20	115.0 (3)
C6—C5—C4	117.5 (3)	C22—C23—C31	120.2 (3)

C7—C5—C4	118.6 (3)	C24—C23—C31	120.9 (3)
C5—C6—C1	124.6 (3)	O7A—C27—C11	109.4 (5)
C8—C7—C5	120.1 (3)	O7B—C27—C11	105.3 (4)
C12—C7—C5	120.1 (3)	O8—C28—C16	112.2 (3)
O5—C8—C7	121.3 (3)	O11—C31—C23	108.4 (3)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
O5—H5···O4	2.25	2.974 (4)	143
O7A—H7A···O8^i	1.95	2.793 (8)	174
O7B—H7B···O8^i	2.00	2.833 (7)	166
O8—H8···O7A^{ii}	1.98	2.793 (8)	159
O8—H8···O7B^{ii}	1.99	2.833 (7)	176
O11—H11···O5^{iii}	1.92	2.772 (3)	175

Symmetry codes: (i) $\frac{1}{2} + x, \frac{3}{2} - y, -z$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, -z$; (iii) $x - \frac{1}{2}, y, \frac{1}{2} - z$.

The structure was determined by direct methods. H atoms were added at calculated positions and refined isotropically using a riding model. H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached. All other non-H atoms were refined anisotropically, except for the disordered O7. The hydroxyl group O7—H7 has two orientations with occupancies of 0.48 (1) and 0.52 (1).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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1,2-Diacetyl-4-phenyl-1,2,4-triazolidine-3,5-dione

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Abstract

The title crystal, $C_{12}H_{11}N_3O_4$, contains three essentially identical molecules in the asymmetric unit. The triazole rings in the three independent molecules are planar within 0.014 Å. The N atom containing the phenyl substituent is trigonal, the sum of the three bond angles being 359.5°. The other two N atoms are slightly pyramidal, the sum of the three bond angles being 346°. The two acetyl groups are twisted out of the plane of the triazole ring by an average of 33° and are *trans* to each other.

Comment

The structure determination of the title compound, (I) (Simlot, Izydore, Wong & Hall, 1994), was undertaken to establish its conformation and compare it with the previously determined conformation of 1,2-diacetyl-4,4-diethyl-3,5-pyrazolidinedione (Izydore, Bernal-Ramirez & Singh, 1990). As with the pyrazolidinedione, the acetylation in the present triazole takes place at the N atoms.

(I)
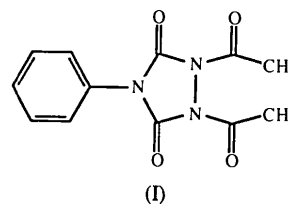
The crystal structure has a curious feature in that it contains six molecules in a triclinic unit cell and, therefore, three independent molecules in the asymmetric unit of space group $P\bar{1}$. Although the cell-reduction routine provided with the diffractometer is quite reliable, we have further confirmed the absence of any symmetry higher than triclinic using the NRC cell-reduction program *CREDUC* (Le Page, 1982). No other efforts were made to look for higher symmetry.

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