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# Lignin Model Compounds: 4,4′-*O*-Dimethyldehydrodiacetovanillone and 4,4′-*O*-Diethyldehydrodiacetovanillone

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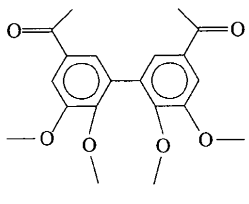
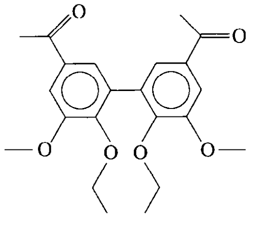
## Abstract

The title compounds, 5,5′-diacetyl-2,2′,3,3′-tetramethoxy-1,1′-biphenyl, $C_{20}H_{22}O_6$, and 5,5′-diacetyl-2,2′-diethoxy-3,3′-dimethoxy-1,1′-biphenyl (IUPAC nomenclature), $C_{22}H_{26}O_6$, correspond to the 5,5′-biphenyl-type lignin model compound. They were synthesized from dehydrodiacetovanillone by alkylation with $CH_3I$ and $C_2H_5I$. In the former compound, all non-H atoms in the asymmetric unit are planar except for one C atom. In the latter compound, there are two molecules of different conformations, one of which is affected by disorder.

## Comment

Lignin is a macromolecule which causes paper to yellow with age. It is a by-product of the cellulose industry and represents an important source for the production of aromatic substances. The main route for elucidation of the complex lignin structure has been the synthesis of small molecules followed by comparative NMR and IR studies of the model compound prepared and the lignin (Hergert, 1971; Drumond *et al.*, 1989, 1992). Structure determination by diffraction techniques can be helpful in interpreting NMR and IR spectra. The title compounds, (I) and (II), described herein were synthesized with the aim of studying dimeric model compounds related to 5,5′-arylpropanoid substructures (biphenyl derivatives) frequently found in lignins (Sarkanen & Ludwing, 1971; Adler, 1977; Chen, 1991).


(I)


(II)

The structure of 4,4′-*O*-dimethyldehydrodiacetovanillone, (I), is shown in Fig. 1. Half of the molecule constitutes an asymmetric unit. The average deviation of the aromatic ring C atoms from the best least-squares plane through the rings is 0.010 (2) Å. The dihedral angle between the two aromatic ring planes is 60.00 (7)°. All of the non-H atoms in the asymmetric unit are almost planar, except for C10, which deviates by 1.291 (3) Å from the best least-squares plane.

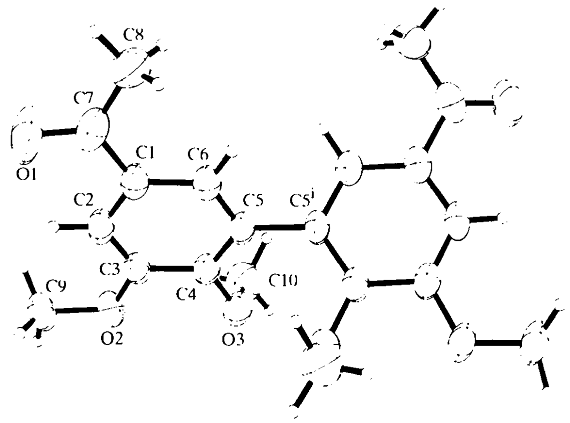


Fig. 1. The molecular structure of 4,4′-*O*-dimethyldehydrodiacetovanillone with ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x, y, -z+\frac{1}{2}$.]

The structure of compound (II), 4,4′-*O*-diethyldehydrodiacetovanillone, is shown in Fig. 2. There are two molecules of different conformations in the asymmetric unit. The C(ring)—O(methoxy and/or ethoxy) bonds have a mean length of 1.371 (6) Å (external standard deviation estimate, *i.e.* calculated from the scatter of the data). The average bond distances and angles in the aromatic rings are 1.389 (9) Å and 120 (1)°, respectively. As expected, the four aromatic rings are planar, the maximum deviation from the best least-squares plane being 0.022 (2) Å. The dihedral angles between the aromatic rings are 114.9 (2) and 60.2 (1)° in molecules *A* and *B*, respectively. The structure of the *B* isomer is analogous to that of compound (I).

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† Deceased January 10, 1997.

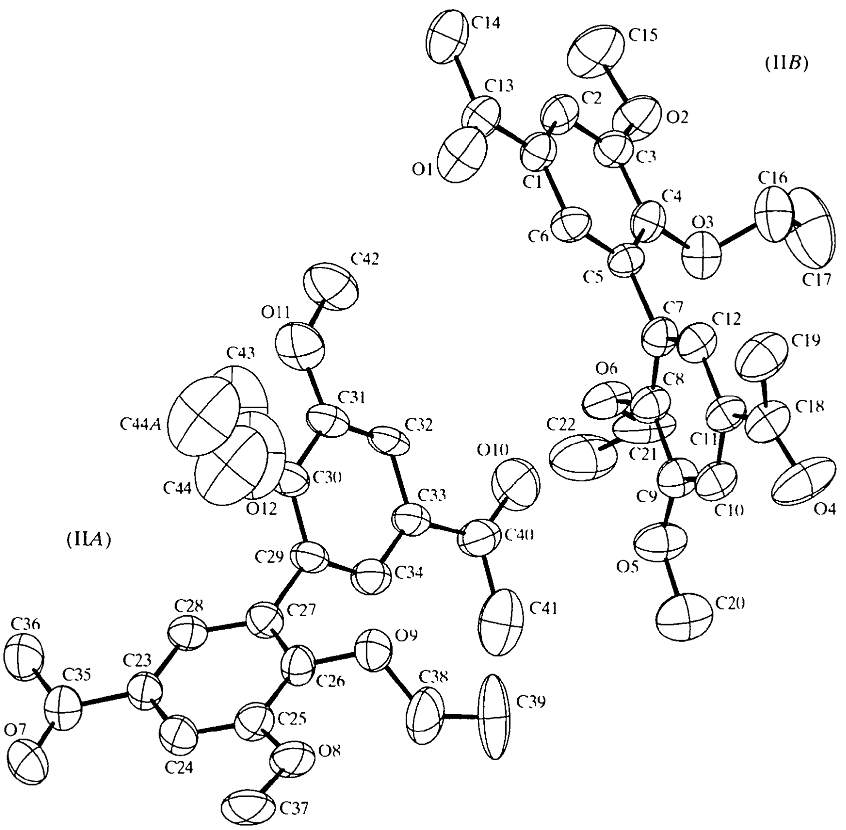

Fig. 2. Molecular structures of the *A* and *B* isomers of 4,4′-*O*-diethyldehydrodiacetovanillone with ellipsoids drawn at the 50% probability level.

## Experimental

The syntheses of (I) and (II) were performed in two steps. Firstly, a dehydrogenative coupling of acetovanillone occurred in the presence of $Fe_2SO_4$ and $K_2S_2O_8$ to form dehydrodiacetovanillone (Drumond *et al.*, 1992). Secondly, a Williamson synthesis was undertaken by reacting dehydrodiacetovanillone with $CH_3I/K_2CO_3$ [to give (I)] and $CH_3CH_2I/K_2CO_3$ [to give (II)] in dimethylformamide. Single crystals were obtained by slow evaporation from ethanol solution.

### Compound (I)

*Crystal data*

$C_{20}H_{22}O_6$
$M_r = 358.38$
Monoclinic
$C2/c$
$a = 20.090\,(2)$ Å
$b = 7.0879\,(6)$ Å
$c = 15.414\,(1)$ Å
$\beta = 124.513\,(4)°$
$V = 1808.6\,(4)$ Å$^3$
$Z = 4$
$D_x = 1.316$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 27 reflections
$\theta = 5.0–12.0°$
$\mu = 0.10$ mm$^{-1}$
$T = 298$ K
Prism
$0.45 \times 0.40 \times 0.10$ mm
Colourless

*Data collection*

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (Lundgren, 1982)
$T_{\min} = 0.960$, $T_{\max} = 0.986$
3337 measured reflections
2652 independent reflections
2652 reflections with $I > 0$

$R_{\rm int} = 0.019$
$\theta_{\max} = 30.00°$
$h = -1 \rightarrow 28$
$k = -1 \rightarrow 10$
$l = -21 \rightarrow 18$
3 standard reflections every 297 reflections
intensity decay: <1%

*Refinement*

Refinement on $F^2$
$R(F^2)(F^2 > 0) = 0.060$
$wR(F^2)(F^2 > 0) = 0.089$
$S(F^2)(F^2 > 0) = 1.851$
2652 reflections
153 parameters
All H atoms refined
$w = 1/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\max} = 0.015$
$\Delta\rho_{\max} = 0.183$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.140$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (I)*

| | | | |
|---|---|---|---|
| O1—C7 | 1.212 (2) | C1—C7 | 1.485 (2) |
| O2—C3 | 1.364 (2) | C2—C3 | 1.369 (2) |
| O2—C9 | 1.434 (2) | C3—C4 | 1.415 (2) |
| O3—C4 | 1.364 (2) | C4—C5 | 1.383 (2) |

| | | | |
|---|---|---|---|
| O3—C10 | 1.423 (2) | C5—C5ⁱ | 1.490 (2) |
| C1—C2 | 1.390 (2) | C5—C6 | 1.384 (2) |
| C1—C6 | 1.389 (2) | C7—C8 | 1.482 (3) |
| O1—C7—C1 | 120.4 (2) | O3—C4—C5 | 120.6 (1) |
| O1—C7—C8 | 120.5 (2) | C4—O3—C10 | 113.9 (1) |
| O2—C3—C2 | 125.7 (1) | C1—C7—C8 | 119.2 (1) |
| O2—C3—C4 | 114.4 (1) | C2—C1—C7 | 119.5 (1) |
| C3—O2—C9 | 117.3 (1) | C4—C5—C5ⁱ | 121.5 (1) |
| O3—C4—C3 | 119.7 (1) | | |

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

## Compound (II)

*Crystal data*

$C_{22}H_{26}O_6$
$M_r = 386.43$
Triclinic
$P\bar{1}$
$a = 11.4731\ (4)$ Å
$b = 12.2009\ (4)$ Å
$c = 17.6234\ (7)$ Å
$\alpha = 72.477\ (3)°$
$\beta = 75.764\ (3)°$
$\gamma = 62.294\ (2)°$
$V = 2066.30\ (13)$ Å$^3$
$Z = 4$
$D_x = 1.242$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 90 reflections
$\theta = 14.96–18.66°$
$\mu = 0.090$ mm$^{-1}$
$T = 298\ (2)$ K
Transparent block
0.40 × 0.30 × 0.20 mm
Colourless

*Data collection*

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (Lundgren, 1982)
$T_{min} = 0.968$, $T_{max} = 0.981$
6753 measured reflections
5294 independent reflections
3982 reflections with $I > 2\sigma(I)$

$R_{int} = 0.025$
$\theta_{max} = 26.44°$
$h = -1 \rightarrow 12$
$k = -11 \rightarrow 12$
$l = -18 \rightarrow 18$
3 standard reflections every 97 reflections intensity decay: <1%

*Refinement*

Refinement on $F^2$
$R(F)[F > 4\sigma(F)] = 0.049$
$wR(F^2)[F^2 > 2\sigma(F^2)] = 0.056$
$S(F^2)[F^2 > 2\sigma(F^2)] = 2.305$
5294 reflections
528 parameters
H-atom parameters calculated and not refined
$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = -0.002$

$\Delta\rho_{max} = 0.230$ e Å$^{-3}$
$\Delta\rho_{min} = -0.048$ e Å$^{-3}$
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0061 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| O1—C13 | 1.220 (3) | C5—C7 | 1.490 (3) |
| O2—C15 | 1.431 (3) | C11—C18 | 1.501 (4) |
| O3—C16 | 1.444 (3) | C13—C14 | 1.500 (4) |
| O4—C18 | 1.208 (3) | C16—C17 | 1.474 (4) |
| O5—C20 | 1.409 (3) | C18—C19 | 1.491 (4) |
| O6—C21 | 1.473 (3) | C21—C22 | 1.471 (4) |
| O7—C35 | 1.219 (3) | C23—C35 | 1.495 (4) |
| O8—C37 | 1.417 (3) | C27—C29 | 1.499 (3) |
| O9—C38 | 1.435 (3) | C33—C40 | 1.502 (4) |
| O10—C40 | 1.215 (3) | C35—C36 | 1.501 (4) |
| O11—C42 | 1.427 (3) | C38—C39 | 1.427 (4) |
| O12—C30 | 1.378 (3) | C40—C41 | 1.495 (4) |
| O12—C43 | 1.449 (5) | C43—C44 | 1.412 (6) |
| O12—C43*A* | 1.450 (5) | C43*A*—C44*A* | 1.412 (6) |
| C1—C13 | 1.492 (4) | | |
| C3—O2—C15 | 118.0 (2) | C19—C18—C11 | 119.3 (3) |
| C4—O3—C16 | 115.5 (2) | C22—C21—O6 | 107.0 (3) |
| C9—O5—C20 | 118.3 (2) | C28—C23—C35 | 122.2 (2) |
| C8—O6—C21 | 116.7 (2) | O8—C25—C24 | 125.0 (2) |
| C25—O8—C37 | 117.9 (2) | O9—C26—C27 | 118.5 (2) |
| C26—O9—C38 | 115.0 (2) | C26—C27—C29 | 121.4 (2) |
| C31—O11—C42 | 117.6 (2) | C30—C29—C27 | 120.4 (2) |
| C30—O12—C43 | 124.3 (7) | C29—C30—O12 | 120.3 (2) |
| C6—C1—C13 | 118.3 (2) | O12—C30—C31 | 118.7 (2) |
| O2—C3—C2 | 124.7 (2) | O11—C31—C32 | 125.0 (3) |
| O3—C4—C5 | 119.5 (2) | C34—C33—C40 | 123.1 (3) |
| C6—C5—C7 | 119.2 (2) | O7—C35—C23 | 120.8 (3) |
| C8—C7—C5 | 122.0 (2) | C23—C35—C36 | 119.1 (3) |
| O6—C8—C7 | 118.7 (2) | C39—C38—O9 | 110.9 (3) |
| O5—C9—C10 | 124.2 (2) | O10—C40—C41 | 120.3 (3) |
| C12—C11—C18 | 122.9 (2) | C41—C40—C33 | 119.5 (3) |
| O1—C13—C1 | 119.8 (2) | C44—C43—O12 | 103.3 (8) |
| C1—C13—C14 | 120.5 (3) | C44*A*—C43*A*—O12 | 117.4 (7) |
| O4—C18—C19 | 120.7 (3) | | |

For (I), refinements and all subsequent calculations were performed on a VAX computer using the *DUPALS* package of crystallographic programs (Lundgren, 1982). The H atoms were found from $\Delta\rho$ maps. The positional parameters were refined for all atoms, including H atoms; anisotropic displacements were refined for non-H atoms. For the H atoms, two different isotropic displacements were refined, one for ring H atoms and one for methyl H atoms. The H atoms in (II) were placed in idealized positions. Positional and anisotropic displacement parameters were refined for all non-H atoms; parameters for H atoms were fixed. In the course of the refinement, it soon became evident that the C atoms of the ethoxy group O12—C43—C44 were disordered. Alternative sites for C43 and C44 were therefore found in the Fourier maps, and it was then possible to improve the model and geometrical parameters such as bond distances, angles and *R* value. The sum of the occupancy factors for the C43—C44 and C43*A*—C44*A* groups were restrained to unity; for C43—C44 the refined value was 0.457 (6). The anisotropic displacements of C43 and C43*A* were restrained to be equal. A similar restriction was applied to C44 and C44*A*.

For both compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *XS* in *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structures: *DUPALS* for (I); *SHELXL*93 (Sheldrick, 1993) for (II). Molecular graphics: *XP* in *SHELXTL/PC* for (I); *ORTEP*II (Johnson, 1976) for (II). Software used to prepare material for publication: *XPUBL* in *SHELXTL/PC* for (I); MS-DOS6.22 Editor for (II).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1044). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). **C54**, 840–842

# Hydrogen Bonding in the 1:1 Adduct of 1,10-Phenanthroline and 1,1′-Binaphthyl-2,2′-diol

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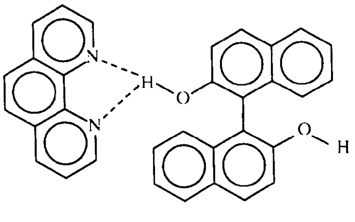
*(Received 7 October 1997; accepted 22 December 1997)*

## Abstract

The title compound, $C_{12}H_8N_2.C_{20}H_{14}O_2$, was obtained as a 1:1 adduct from non-aqueous solutions of the two components. The lattice contains centrosymmetric dimers in which O—H···O and O—H···N hydrogen bonding is important. Rotation about the C—C′ bond of the binaphthyl moiety produces a torsion angle of −85.5 (2)°.

## Comment

The title compound, (I), was identified initially during work on the direct electrochemical synthesis of metal derivatives of 1,1′-binaphthyl-2,2′-diol (binaphthol) and related enolic compounds (García-Martínez & Tuck, 1997). It was subsequently shown that the same material could be produced by the evaporation of equimolar solutions in various non-aqueous solvents.



(I)

The structure of the adduct is shown in Fig. 1. Selected geometric parameters are given in Table 1 and hydrogen-bonding details are given in Table 2. Crystals were obtained from three different solvents ($CH_3OH$, $C_2H_5OH$ and $CH_2Cl_2$) and, in each case, the cell parameters were measured, showing that the three sets of crystals were identical within experimental error.

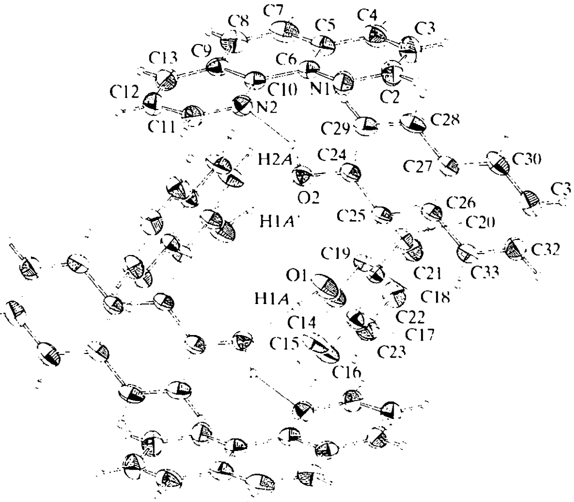


Fig. 1. *ZORTEP* (Zsolnai, 1994) diagram of $C_{12}H_8N_2.C_{20}H_{14}O_2$ showing the numbering system. Atoms are represented as displacement ellipsoids drawn at the 30% probability level.

The structures of binaphthol and its derivatives have been of interest because of the use of such molecules in the optical resolution of asymmetric species (Cram & Cram, 1979). The structures of both the (+)-(*R*)- and racemic forms have been reported by Mori *et al.* (1993). Immediate points of comparison with the title compound are the (O)C—C—C—C(O) torsion angles, which are −76.731 and −88.266°, respectively, in the (+)-(*R*)- and racemic molecules [data obtained from the Cambridge Structural Database (Allen & Kennard, 1993)], and −85.5 (2)° (C14—C19—C25—C24) for the binaphthol moiety in the present case, but in the parent binaphthol structures, the OH groups are *cis*, in