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Acta Cryst. (1998). **C54**, 837–840

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

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(Received 21 April 1997; accepted 27 November 1997)

Abstract

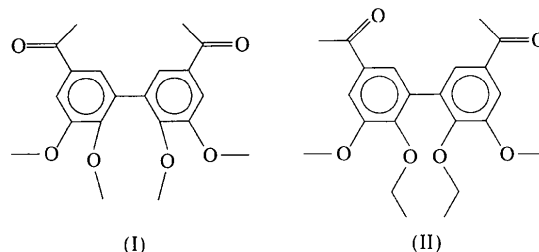
The title compounds, 5,5'-diacetyl-2,2',3,3'-tetramethoxy-1,1'-biphenyl, $C_{20}H_{22}O_6$, and 5,5'-diacetyl-2,2'-diethoxy-3,3'-dimethoxy-1,1'-biphenyl (IUPAC nomenclature), $C_{22}H_{26}O_6$, correspond to the 5,5'-biphenyl-type lignin model compound. They were synthesized from dehydrodiacetovanillone 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,

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(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).



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.

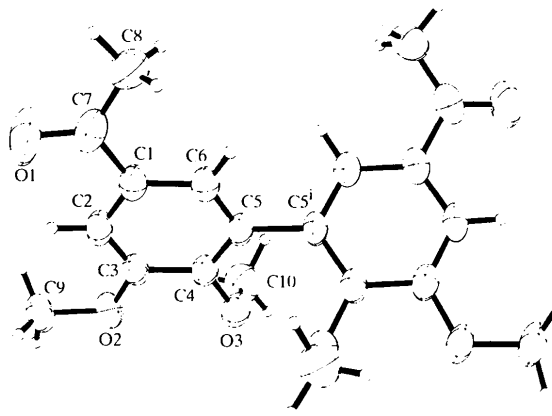


Fig. 1. The molecular structure of 4,4'-*O*-dimethyldehydrodiacetovanillone with ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.]

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).

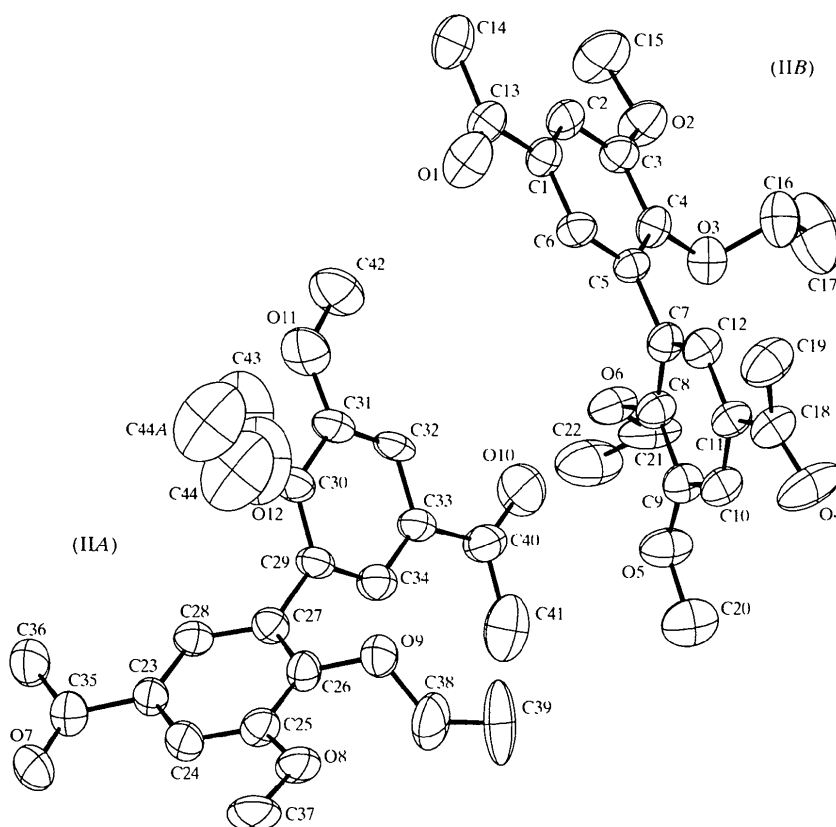


Fig. 2. Molecular structures of the A and B isomers of 4,4'-O-diethyldehydrodiacetovanillone with ellipsoids drawn at the 50% probability level.

Experimental

The syntheses of (I) and (II) were performed in two steps. Firstly, a dehydrogenative coupling of acetovanillone occurred in the presence of Fe₂SO₄ and K₂S₂O₈ to form dehydrodiacetovanillone (Drumond *et al.*, 1992). Secondly, a Williamson synthesis was undertaken by reacting dehydrodiacetovanillone with CH₃I/K₂CO₃ [to give (I)] and CH₃CH₂I/K₂CO₃ [to give (II)] in dimethylformamide. Single crystals were obtained by slow evaporation from ethanol solution.

Compound (I)

Crystal data

C₂₀H₂₂O₆
M_r = 358.38
 Monoclinic
*C*2/*c*
a = 20.090 (2) Å
b = 7.0879 (6) Å
c = 15.414 (1) Å
 β = 124.513 (4)°
V = 1808.6 (4) Å³
Z = 4
D_x = 1.316 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 27 reflections
 θ = 5.0–12.0°
 μ = 0.10 mm⁻¹
T = 298 K
 Prism
 0.45 × 0.40 × 0.10 mm
 Colourless

Data collection

Siemens *P4* 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_{int} = 0.019
 θ_{max} = 30.00°
 h = -1 → 28
 k = -1 → 10
 l = -21 → 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
 $w = 1/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\text{max}}$ = 0.015
 $\Delta\rho_{\text{max}}$ = 0.183 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -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—C5'	1.490 (2)	O7—C35	1.219 (3)	C23—C35	1.495 (4)
C1—C2	1.390 (2)	C5—C6	1.384 (2)	O8—C37	1.417 (3)	C27—C29	1.499 (3)
C1—C6	1.389 (2)	C7—C8	1.482 (3)	O9—C38	1.435 (3)	C33—C40	1.502 (4)
O1—C7—C1	120.4 (2)	O3—C4—C5	120.6 (1)	O10—C40	1.215 (3)	C35—C36	1.501 (4)
O1—C7—C8	120.5 (2)	C4—O3—C10	113.9 (1)	O11—C42	1.427 (3)	C38—C39	1.427 (4)
O2—C3—C2	125.7 (1)	C1—C7—C8	119.2 (1)	O12—C30	1.378 (3)	C40—C41	1.495 (4)
O2—C3—C4	114.4 (1)	C2—C1—C7	119.5 (1)	O12—C43	1.449 (5)	C43—C44	1.412 (6)
C3—O2—C9	117.3 (1)	C4—C5—C5'	121.5 (1)	O12—C43A	1.450 (5)	C43A—C44A	1.412 (6)
O3—C4—C3	119.7 (1)			C1—C13	1.492 (4)		

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

Compound (II)

Crystal data

$C_{22}H_{26}O_6$

$M_r = 386.43$

Triclinic

$P\bar{1}$

$a = 11.4731 (4) \text{ \AA}$

$b = 12.2009 (4) \text{ \AA}$

$c = 17.6234 (7) \text{ \AA}$

$\alpha = 72.477 (3)^\circ$

$\beta = 75.764 (3)^\circ$

$\gamma = 62.294 (2)^\circ$

$V = 2066.30 (13) \text{ \AA}^3$

$Z = 4$

$D_x = 1.242 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Siemens P4 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

$I > 2\sigma(I)$

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

$w = 1/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\max} = -0.002$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 90
reflections

$\theta = 14.96\text{--}18.66^\circ$

$\mu = 0.090 \text{ mm}^{-1}$

$T = 298 (2) \text{ K}$

Transparent block

$0.40 \times 0.30 \times 0.20 \text{ mm}$

Colourless

$R_{\text{int}} = 0.025$

$\theta_{\max} = 26.44^\circ$

$h = -1 \rightarrow 12$

$k = -11 \rightarrow 12$

$l = -18 \rightarrow 18$

3 standard reflections

every 97 reflections

intensity decay: $< 1\%$

$\Delta\rho_{\max} = 0.230 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.048 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick,
1993)

Extinction coefficient:

0.0061 (2)

Scattering factors from

International Tables for
Crystallography (Vol. C)

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)	C44A—C43A—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 C43A—C44A groups were restrained to unity; for C43—C44 the refined value was 0.457 (6). The anisotropic displacements of C43 and C43A were restrained to be equal. A similar restriction was applied to C44 and C44A.

For both compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *XS* in *SHELXTLPC* (Sheldrick, 1990). Program(s) used to refine structures: *DUPALS* for (I); *SHELXL93* (Sheldrick, 1993) for (II). Molecular graphics: *XP* in *SHELXTLPC* for (I); *ORTEPII* (Johnson, 1976) for (II). Software used to prepare material for publication: *XPUBL* in *SHELXTLPC* for (I); MS-DOS6.22 Editor for (II).

Financial support from the Minas Gerais Foundation for Research Development (FAPEMIG) is gratefully acknowledged (Grant CEX 1123/90).

Table 2. Selected geometric parameters ($\text{\AA}$, $^\circ$) 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)

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)

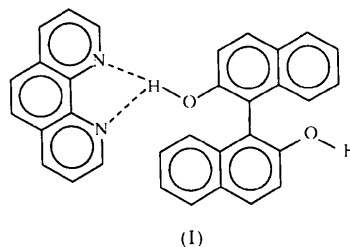
Abstract

The title compound, C₁₂H₈N₂·C₂₀H₁₄O₂, 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.



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 (CH₃OH, C₂H₅OH and CH₂Cl₂) and, in each case, the cell parameters were measured, showing that the three sets of crystals were identical within experimental error.

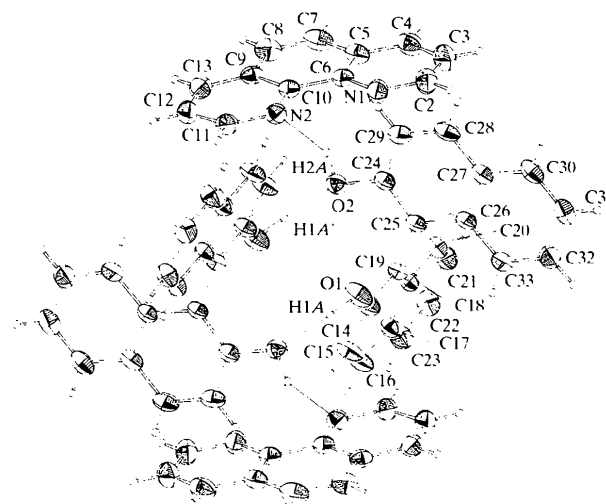


Fig. 1. ZORTEP (Zsolnai, 1994) diagram of C₁₂H₈N₂·C₂₀H₁₄O₂ showing the numbering system. Atoms are represented as displacement ellipsoids drawn at the 30% probability level.

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(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