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### 7-(4-Hydroxy-3-methoxyphenyl)-6-hydroxymethyl-4,10-dimethoxy-2,8-dipropyl-*cis*-6,7-dihydrodibenzo[*b,d*]oxepin-11-ol

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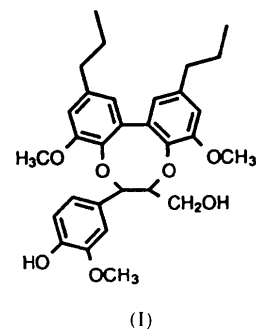
#### Abstract

The title compound, C<sub>30</sub>H<sub>36</sub>O<sub>7</sub>, has a dibenzoxepine structure formed by acid treatment of a lignin model compound with a dibenzodioxocine structure.

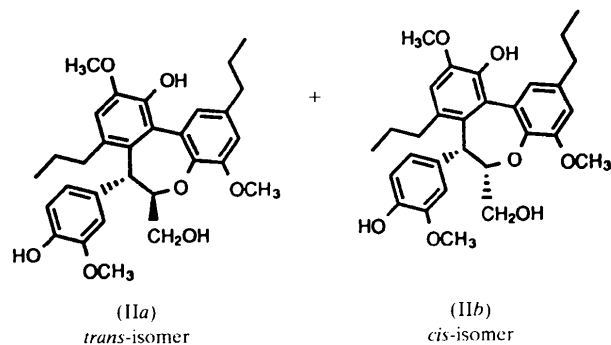
#### Comment

Dibenzodioxocines are novel 'neolignans' involving an eight-membered ring system formed in an oxidative coupling reaction of an *o,o'*-dihydroxybiphenyl structure with coniferyl alcohol (Karhunen *et al.*, 1995a). These structural units have been shown to be present in softwood lignins (Karhunen *et al.*, 1995b; Ralph *et al.*, 1997). The elucidation of the chemical behaviour of lignin, especially in degradation procedures, is greatly

facilitated by studying the behaviour of appropriate model compounds under degradative conditions. In order to investigate the reactivity of the dibenzodioxocine structures, hydrolytic reactions have been carried out with compound (I). Under acidic conditions, the main product is observed to have a dibenzoxepine structure, probably formed *via* a benzyl cation (Karhunen *et al.*, 1996). Two isomeric products have been isolated, (IIa) (major) and (IIb) (minor). The NMR data of (IIa) and (IIb), and the crystal structures of (IIa) (peracetate) and (III) have been reported previously (Karhunen *et al.*, 1996). We report here the structure of the *cis*-isomer, (IIb).



(I)

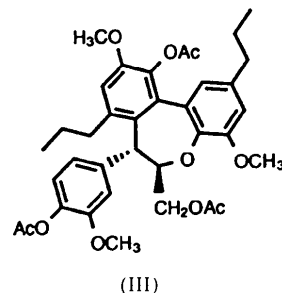


(IIa)

trans-isomer

(IIb)

cis-isomer



(III)

The geometry and numbering scheme of the title molecule are shown in Fig. 1. The most interesting part of the molecule is the seven-membered ring, which is in the boat conformation. Atoms C7, C14 and C19 are above the mean plane defined by atoms C8, C13,

C20 and O1. The change of the substitution from *trans* in (III) to *cis* in (IIb) retains the boat conformation, but is reflected in the bond angles and torsion angles of the ring. Major differences are around the C7 and C20 atoms. The torsion angles C8—C7—C20—O1 and C19—O1—C20—C7 of  $-30.6(5)$  and  $-55.4(4)^\circ$ , respectively, in compound (III), change to  $-52.8(3)$  and  $-26.4(3)^\circ$  in compound (IIb). The presence of the *cis* substituent causes opening of the C19—O1—C20 angle from  $113.4(3)^\circ$  in (III) to  $121.2(2)^\circ$  in (IIb). The conformation of the seven-membered ring is more distorted in the *trans* compound (III). The benzene rings in normal biphenyl structures are at an angle of  $57\text{--}59^\circ$ ; this angle is  $51.4(1)^\circ$  in (III), whereas in (IIb), it is considerably less at  $45.0(3)^\circ$ .

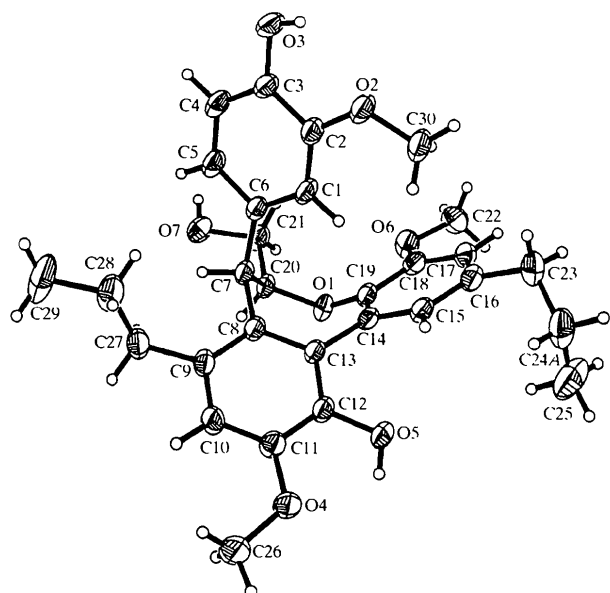


Fig. 1. The molecular geometry and numbering scheme of the title compound. Displacement ellipsoids are plotted at the 30% probability level. Only one orientation of the disordered propyl group is shown.

The molecules are held together by hydrogen bonds between the terminal OH groups to give a three-dimensional network. Hydrogen-bonding details are given in Table 2.

## Experimental

The title compound was obtained by treating compound (1) with dilute HCl in dioxane solution at 323 K under an inert atmosphere (Johansson & Miksche, 1972). After neutralization and extraction with chloroform, the solvent was evaporated and the reaction mixture fractionated by column chromatography. Two diastereomers, (IIa) and (IIb), were isolated in 50 and 17% yields, respectively. Isomer (IIb) was crystallized for X-ray analysis from a mixture of chloroform and pentane at room temperature.

## Crystal data

C<sub>30</sub>H<sub>36</sub>O<sub>7</sub>  
*M<sub>r</sub>* = 508.59  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 9.256 (4) Å  
*b* = 11.917 (4) Å  
*c* = 23.489 (8) Å  
 $\beta$  = 94.74 (3)°  
*V* = 2582.1 (17) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.308 Mg m<sup>-3</sup>  
*D<sub>m</sub>* = 1.31 (2) Mg m<sup>-3</sup>  
*D<sub>m</sub>* measured by flotation

## Data collection

Rigaku AFC-7S diffractometer  
 2 $\theta$ / $\omega$  scans  
 Absorption correction: none  
 4765 measured reflections  
 4523 independent reflections  
 3547 reflections with  $I > 2\sigma(I)$

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.064  
*wR*(*F*<sup>2</sup>) = 0.194  
*S* = 0.927  
 4523 reflections  
 344 parameters  
 H atoms riding  
 $w = 1/[\sigma^2(F_o^2) + (0.1459P)^2 + 1.2408P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 8.14–12.76°  
 $\mu$  = 0.092 mm<sup>-1</sup>  
*T* = 193 (2) K  
 Prismatic  
 0.45 × 0.30 × 0.25 mm  
 Pale yellow

*R*<sub>int</sub> = 0.027  
 $\theta_{\max}$  = 25.02°  
*h* = 0 → 11  
*k* = 0 → 14  
*l* = -27 → 27  
 3 standard reflections every 200 reflections  
 intensity decay: none

( $\Delta/\sigma$ )<sub>max</sub> = 0.045  
 $\Delta\rho_{\max}$  = 0.318 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.344 e Å<sup>-3</sup>  
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C19	1.375 (3)	C8—C13	1.425 (3)
O1—C20	1.447 (3)	C13—C14	1.485 (3)
C7—C8	1.527 (3)	C14—C19	1.391 (3)
C7—C20	1.535 (3)		
C19—O1—C20	121.2 (2)	C19—C14—C13	120.6 (2)
C8—C7—C20	110.0 (2)	O1—C19—C14	121.7 (2)
C13—C8—C7	121.1 (2)	O1—C20—C7	116.8 (2)
C8—C13—C14	122.0 (2)		
C20—C7—C8—C13	62.6 (3)	C13—C14—C19—O1	-10.0 (3)
C7—C8—C13—C14	5.6 (3)	C19—O1—C20—C7	-26.4 (3)
C8—C13—C14—C19	-43.8 (3)	C8—C7—C20—O1	-52.8 (3)
C20—O1—C19—C14	68.2 (3)		

Table 2. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H... <i>A</i>	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3A...O7 <sup>i</sup>	2.092	2.809 (3)	142
O5—H5A...O1 <sup>ii</sup>	2.309	3.133 (3)	163
O7—H7A...O3 <sup>iii</sup>	1.980	2.829 (3)	176

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

H atoms were refined using a riding model, with *U*<sub>iso</sub> 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. The propyl group C23—C25 has two orientations with occupancies of 0.78 (1) and 0.22 (1).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993b). 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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1215). Services for accessing these data are described at the back of the journal.

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## An Orthorhombic Polymorph of 2,2'-Dipyridyl Diselenide†

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### Abstract

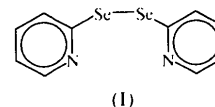
X-ray analysis has established the crystal structure of a non-centrosymmetric polymorph of 2,2'-dipyridyl diselenide, C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>Se<sub>2</sub>, at ambient temperature. The molec-

† Alternative name: 2,2'-diselenodipyridine.

ular structure is very similar to the low-temperature structure of the centrosymmetric monoclinic form reported recently. The crystal packing in the two polymorphs is compared.

### Comment

As part of an ongoing study of the dipyridyl chalcogenides exploring the factors governing the geometry of dichalcogenide linkages, we have determined the crystal structure of an orthorhombic polymorph of 2,2'-dipyridyl diselenide, (1), recrystallized from petroleum ether (b.p. 313–343 K). A non-centrosymmetric space group was indicated clearly by the statistical averages for the normalized structure amplitudes, for which the experimental  $\langle |E^2 - 1| \rangle$  value was 0.740 (Karle *et al.*, 1965). This was subsequently confirmed by successful refinement in the non-centrosymmetric space group *Pna2*<sub>1</sub>. After we had completed our analysis, we became aware of a report of the crystal structure of a monoclinic form at 173 K (Kienitz *et al.*, 1996). The crystals of the monoclinic form were grown from diethyl ether/light petroleum (b.p. 303–313 K) at 243 K, and belonged to the centrosymmetric space group *P2*<sub>1</sub>/*c*. We report here the crystal structure of the orthorhombic polymorph and compare it with that of the monoclinic form.



The molecular structures of the polymorphs are almost identical. The C—Se—Se—C torsion angles are 84.3(2) and –83.6(3)° in the monoclinic and orthorhombic forms, respectively, and the Se—Se bonds lie close to each pyridyl ring plane. In fact, in the monoclinic structure the two bonds lie within the ring planes as indicated by the torsion angles Se'—Se—C2—C3 –0.8(6)° and Se—Se'—C2'—C3' 0.6(5)°. In the orthorhombic structure, the Se—Se bond lies within one of the ring planes [torsion angle Se1—Se1'—C2'—C3' 0.6(6)°], but it is significantly displaced from the other ring plane [Se1'—Se1—C2—C3 4.7(6)°]. This appears to be the major conformational difference between the two polymorphs and must be a consequence of the different packing modes in the two crystal forms. It is of interest to note that in diphenyl diselenide the two torsion angles are 2.4 and 23.9° (Marsh, 1952) and in 4,4'-dinitrophenyl diselenide the Se—Se bond is significantly displaced from each aromatic plane as reflected in the torsion angles of 23.3° (Morris & Einstein, 1986); those of all other reported diaryl diselenides lie in the range 55–90°. A coplanar arrangement of the rings and the Se—Se bond should minimize unfavourable repulsions between the Se atom lone pairs and the  $\pi$ -electron system of the aromatic