grant and funds for an X-ray diffractometer to JWQ. In addition, the Canadian Commonwealth Scholarship and Fellowship Plan provided financial assistance to SNP, allowing him to study at the University of Saskatchewan. Nordic Merrell Dow Research Canada is thanked for providing a grant to JRD.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1069). Services for accessing these data are described at the back of the journal.

References

Boyd, M. R. & Paull, K. D. (1995). *Drug Dev. Res.* **34**, 91–109.
Brugidou, J. & Christol, H. (1966). *Bull. Soc. Chim. Fr.* pp. 1693–1698.
Brugidou, J., Christol, H. & Sachetto, J. P. (1967). *Bull. Soc. Chim. Fr.* pp. 2579–2584.
Carey, F. A. & Sundberg, R. J. (1977). *Advanced Organic Chemistry*, Part B, p. 46. New York: Plenum Press.
Dimmock, J. R., Pandeya, S. N., Allen, T. M. & Kao, G. Y. (1998). *Pharmazie*, **53**, 201–202.
Enraf–Nonius (1992). *CAD-4 EXPRESS*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Hall, S. R., King, G. S. D. & Stewart, J. M. (1997). Editors. *Xtal3.5 User's Manual*. University of Western Australia, Australia.
Mühlstädt, M. & Gensrich, H. J. (1966). *J. Prakt. Chem.* **34**, 139–144.
North, A. C. T., Phillips, D. C. & Mathews, F. C. (1968). *Acta Cryst.* A**24**, 351–359.
Phillips, O. A., Nelson, L. A., Knaus, E. E., Allen, T. M. & Fathi-Afshar, R. (1989). *Drug Des. Deliv.* **4**, 121.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1999). C**55**, 1351–1353

(*S*)-2,2′-Bis(methoxymethoxy)[1,1′-binaphthyl]-3,3′-dicarbaldehyde

Yoshimitsu Tachi,[a] Shinya Nakayama,[a] Fumito Tani,[a] Go Ueno[b] and Yoshinori Naruta[a]

[a]*Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Higashiku, Fukuoka, 812-8581, Japan, and* [b]*X-ray Research Laboratory, Rigaku Corporation, Matsubara, Akishima, Tokyo, 196-0003, Japan. E-mail: naruta@ms.ifoc.kyushu-u.ac.jp*

(*Received 5 February 1999; accepted 30 March 1999*)

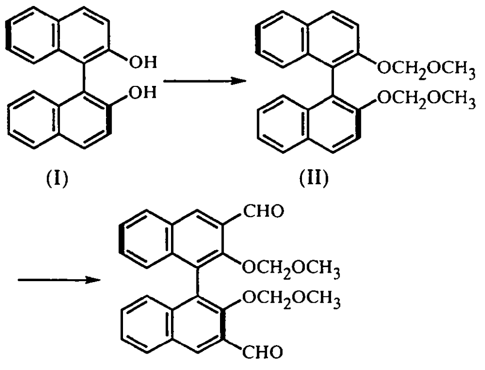
Abstract

The two naphthalene rings of the title compound, $C_{26}H_{22}O_6$, are in a *transoid* conformation. The dihedral angle between the mean planes of the naphthalene rings is large at 107.1 (3)°.

Comment

Optically active 1,1′-binaphthalene derivatives have been widely used in asymmetric reaction as chiral auxiliaries (Rosini *et al.*, 1992; Noyori, 1994). One of their advantages is that the dihedral angles between the two naphthalene ring systems have enough flexibility and adapt to the complexation with various metal ions. To some extent, the molecules can avoid possible steric repulsion by varying their dihedral angles. Their conformation has been analysed in solution using circular dichroism (Hanazaki & Akimoto, 1972; Mason *et al.*, 1974), and in the solid state by X-ray diffraction (Akimoto & Iitaka, 1969; Kerr & Robertson, 1969; Harata & Tanaka, 1973; Kuroda & Mason, 1981; Pauptit & Trotter, 1981, 1983; Franzini *et al.*, 1991).

We herein report the crystal structure of an optically active (*S*)-binaphthalene derivative having 2,2′-bis(methoxymethoxy) and 3,3′-dicarbaldehyde groups. The title compound, (III), was prepared in two steps as shown in the scheme from commercially available (*S*)-1,1′-bi-2-naphthol, (I). [A methoxymethoxy (MOM) group is a flexible chain of moderate length, and synthetically useful both for chelating to metal ions and for protecting an hydroxyl group. A formyl group is also a versatile functional group in organic synthesis.]



(I) (II)

(III)

The two naphthalene rings are almost planar with mean deviations of 0.017 (3) and 0.039 (3) Å. The dihedral angle between the least-squares planes of the two rings is 107.1 (3)°. To the best of our knowledge, it is one of the largest values ever reported in the crystal structure of 1,1′-binaphthalene derivatives [*cf.* 103.1 for (*R*)-1,1′-binaphthyl (Kuroda & Mason, 1981) and 111° for 2,2′-dimethoxy-1,1′-binaphthyl (Gridunova *et al.*, 1983)]. Interestingly, the crystals of these three compounds belong to the same space group, $P4_12_12$. Crystal packing of (*R*)-1,1′-binaphthyl was discussed in detail in comparison with that of racemic 1,1′-binaphthyl whose crystal belongs to the *C*2/*c* group (Kuroda & Mason, 1981). This packing is relatively loose, thus causing a larger volume per molecule. It is worth noting that the present crystal also has a long c axis [37.939 (7) Å] and that the volume per molecule is 549.3 (2) Å^3.

One of the methoxymethoxy groups displays disordering of the O2 atom with site-occupancy factors of 0.7 for atom O2 and 0.3 for O2*. Geometrical parameters of both methoxymethoxy groups are given in Table 1. No intermolecular π–π stacking was observed in the crystal structure.

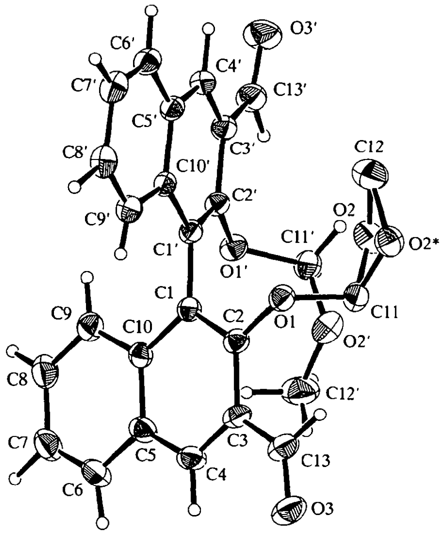


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title molecule showing 20% displacement ellipsoids and the atom-labelling scheme. H atoms of the disordered MOM group have been omitted for clarity.

Experimental

Synthesis of the intermediate (II) bis(methoxymethoxy)-1,1′-binaphthyl: NaH (60% in oil, 4.20 g, 0.110 mol) was placed in a reaction flask and washed twice with dry tetrahydrofuran (THF) (10 ml) under an N_2 atmosphere. To a suspension of the NaH in a mixture of dry THF (150 ml) and dry *N,N*-dimethylformamide (DMF) (40 ml), a dry THF solution (50 ml) of (*S*)-1,1′-bi-2-naphthol (10.1 g, 0.0350 mol) was added dropwise under an N_2 atmosphere at 273 K over 15 min. After stirring for 10 min, chloromethyl methyl ether (10 ml, 0.132 mol) was added dropwise and the resulting mixture was stirred for another 30 min. The reaction mixture was added to ice-water, and then the THF was removed *in vacuo*. The residual aqueous layer was extracted with benzene (3 × 50 ml). The combined organic phase was washed with water and brine, and dried over Na_2SO_4. After evaporation of benzene, the residue was crystallized from CH_2Cl_2–hexane to afford fine, colourless crystals of (II). The crystals were filtered and washed with benzene/hexane (1/5 *v*/*v*) (12.9 g, 0.0345 mol, yield 98%, m.p. 376–378 K). ^{1}H NMR ($CDCl_3$): δ 7.94 (2H, *d*, J = 8.8 Hz, Ar—H), 7.86 (2H, *d*, J = 8.3 Hz, Ar—H), 7.57 (2H, *d*, J = 9.3 Hz, Ar—H), 7.33 (2H, *t*, J = 7.3 Hz, Ar—H), 7.21 (2H, *t*, J = 7.6 Hz, Ar—H), 7.15 (2H, *d*, J = 8.3 Hz, Ar—H), 5.07 (2H, *d*, J = 6.8 Hz, MOM—CH_2), 4.97 (2H, *d*, J = 6.8 Hz, MOM—CH_2), 3.14 p.p.m. (6H, *s*, MOM—CH_3); ^{13}C NMR ($CDCl_3$): δ 152.6, 134.0, 129.8, 129.3, 127.8, 126.2, 125.5, 124.0, 121.2, 117.1, 95.0, 55.7 p.p.m.; High MS [FAB in NBA (4-nitrobenzyl alcohol)] *m*/*z* calculated for $C_{24}H_{22}O_4$ 374.1518; found 374.1513 (M^+); analysis calculated for $C_{24}H_{22}O_4$: C 76.99, H 5.92%; found: C 76.80, H 5.89%.

(*S*)-2,2′-Bis(methoxymethoxy)[1,1′-binaphthyl]-3,3′-dicarbaldehyde, (III): the MOM-protected binaphthyl, (II) (5.01 g, 0.0134 mol), and *N,N,N′,N′*-tetramethylethylenediamine (8 ml, 0.0530 mol) were dissolved in dry ether (350 ml) under an N_2 atmosphere at 273 K. To this solution, 1.6 *N* *n*-butyllithium in hexane (23 ml, 0.0368 mol) was added dropwise over 10 min, and the mixture was stirred overnight. An aliquot of the mixture was then taken and quenched with D_2O, and extracted with ether. The ether layer was dried over $MgSO_4$ and evaporated to dryness. The residue was dissolved in $CDCl_3$ and submitted to ^{1}H NMR measurement. After confirmation of the disappearance of Ar—H3 on a ^{1}H NMR spectrum, distilled DMF (5 ml, 0.0650 mol) was added to the reaction mixture, which was stirred for a further 2 h, then 1 *N* HCl was added to yield a slightly acidic aqueous layer. The mixture was extracted with ethyl acetate (3 × 100 ml), and the combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, and then dried over Na_2SO_4. After evaporation of the solvent, the reaction mixture was crystallized from ether to afford fine, pale yellow crystals. The residual mother liquid was removed, and the crystals were filtered and washed with cold ether and with hexane/ether (6/1 *v*/*v*) (4.17 g, 0.00969 mol, yield 72.4%). Crystals (m.p. 390–392 K) suitable for X-ray analysis were sealed with liquid paraffin in a glass capillary. ^{1}H NMR ($CDCl_3$): δ 10.56 (2H, *s*, CHO), 8.63 (2H, *s*, Ar—H), 8.09 (2H, *d*, J = 7.8 Hz, Ar—H), 7.52 (2H, *t*, J = 7.3 Hz, Ar—H), 7.42 (2H, *t*, J = 7.8 Hz, Ar—H), 7.24 (2H, *d*, J = 8.3 Hz, Ar—H), 4.75 (2H, *d*, J = 6.4 Hz, MOM—CH_2), 4.71 (2H, *d*, J = 6.4 Hz, MOM—CH_2), 2.87 p.p.m. (6H, *s*, MOM—CH_3); ^{13}C NMR ($CDCl_3$): δ 190.5, 154.0, 136.7, 132.3, 130.3, 130.0, 129.6, 128.9, 126.2, 126.1, 125.9, 100.5, 56.9 p.p.m.; High MS (EI) *m*/*z* calculated for $C_{26}H_{22}O_6$ 430.1416, found 430.1427 (M^+); analysis calculated for $C_{26}H_{22}O_6$: C 72.55, H 5.15%; found: C 72.31, H 5.21%.

Crystal data

$C_{26}H_{22}O_6$
M_r = 430.456
Tetragonal
$P4_12_12$
a = 10.764 (3) Å
c = 37.939 (7) Å
V = 4395 (2) Å^3
Z = 8
D_x = 1.301 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 25.6–29.7°
μ = 0.762 mm^{-1}
T = 298.2 K
Prismatic
0.40 × 0.34 × 0.20 mm
Pale yellow

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.731, $T_{\max}$ = 0.840
2566 measured reflections
2566 independent reflections

1932 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 76.33°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 47$
3 standard reflections every 150 reflections intensity decay: 8.59%

Refinement

Refinement on F^2
$R(F) = 0.041$
$wR(F^2) = 0.129$
$S = 1.424$
2526 reflections
300 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + 0.00203(F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: 0.060 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C11	1.451 (4)	O2*—C11	1.30 (1)
O1′—C11′	1.434 (4)	O2*—C12	1.45 (1)
O2—C11	1.385 (6)	O2′—C11′	1.367 (5)
O2—C12	1.340 (7)	O2′—C12′	1.401 (6)
C11—O2—C12	117.1 (6)	O1—C11—O2	111.2 (4)
C11—O2*—C12	115.0 (8)	O1—C11—O2*	111.0 (6)
C11′—O2′—C12′	115.2 (4)	O1′—C11′—O2′	112.3 (3)

The O atom in the disordered methoxymethyl group was refined over two sites (O2 and O2*, occupancies of 0.7 and 0.3, respectively). H atoms, except those of the disordered methoxymethyl group [C11—O2(O2*)—C12] were found by difference Fourier synthesis and constrained with $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$, including H atoms of the major disorder component.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *TEXSAN* and *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *TEXSAN LS* and *SAPI*91. Molecular graphics: *TEXSAN* and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *SAPI*91.

This work was supported by a Grant-in-Aid for COE Research 'Design and Control of Advanced Molecular Assembly Systems' from the Ministry of Education, Science and Culture, Japan (No. 08CE2005).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1308). Services for accessing these data are described at the back of the journal.

References

Akimoto, H. & Iitaka, Y. (1969). *Acta Cryst.* B**25**, 1491–1500.
Fan, H.-F. (1991). *SAPI*91. *Structure Analysis Programs with Intelligent Control.* Rigaku Corporation, Tokyo, Japan.
Franzini, L., Rosini, C. & Pasero, M. (1991). *Acta Cryst.* C**47**, 1259–1261.
Gridunova, G. V., Shklover, V. E., Struchkov, Yu. T. & Chayanov, B. A. (1983). *Kristallografiya*, **28**, 87–91.
Hanazaki, I. & Akimoto, H. (1972). *J. Am. Chem. Soc.* **94**, 4102–4106.
Harata, K. & Tanaka, J. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2747–2751.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kerr, K. A. & Robertson, J. M. (1969). *J. Chem. Soc. B*, pp. 1146–1149.
Kuroda, R. & Mason, S. F. (1981). *J. Chem. Soc. Perkin Trans.* 2, pp. 167–170.
Mason, S. F., Seal, R. H. & Roberts, D. R. (1974). *Tetrahedron*, **30**, 1671–1682.
Molecular Structure Corporation (1995). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1996). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Noyori, R. (1994). In *Asymmetric Catalysis in Organic Synthesis.* New York: Wiley & Sons.
Pauptit, R. A. & Trotter, J. (1981). *Can. J. Chem.* **59**, 1149–1152.
Pauptit, R. A. & Trotter, J. (1983). *Can. J. Chem.* **61**, 69–71.
Rosini, C., Franzini, L., Raffaelli, A. & Salvadori, P. (1992). *Synthesis*, pp. 503–517.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1999). C**55**, 1353–1355

1-D-1,2:5,6-Di-*O*-isopropylidene-3-*O*-(diphenylphosphinoyl)-*chiro*-inositol, a hydrogen-bonded dimeric structure

Andrew Falshaw, Graeme J. Gainsford and Cornelis Lensink

Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand. E-mail: c.lensink@irl.cri.nz

(*Received 10 August 1998; accepted 12 May 1999*)

Abstract

The title compound ($C_{24}H_{29}O_7P$) was prepared from the reaction of chlorodiphenylphosphine with 1-D-1,2:5,6-di-*O*-isopropylidene-*chiro*-inositol in pyridine. The structure consists of two independent molecules of 1-D-1,2:5,6-di-*O*-isopropylidene-3-*O*-(diphenylphosphinoyl)-*chiro*-inositol hydrogen bonded to each other, so that the dimer has close to centrosymmetric symmetry in space group $P1$. Subtle twisting in the fused cyclohexane rings and at the P atoms breaks the centrosymmetry, allowing the formation of strong hydrogen bonds (P═O···H—O 1.9 and 2.0 Å).

Comment

The current interest in the use of carbohydrate molecules as asymmetric ligand fragments for homogeneous catalysis (Gilbertson & Chang, 1995; RajanBabu *et al.*, 1994) prompted us to investigate the use of D-*chiro*-inositol for this purpose. In the course of our work, we isolated the title compound, (I), and report its molecular structure here. The structure consists of two independent molecules of 1-D-1,2:5,6-di-*O*-isopropylidene-3-*O*-(diphenylphosphinoyl)-*chiro*-inositol hydrogen bonded to each other *via* the free phosphate O atoms and