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The crystal structure of (1*R**,2*S**)-1,2-bis(2-fluorophenyl)-3,8-dimethoxyacenaphthene-1,2-diol, C₂₆H₂₀F₂O₄

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Abstract

C₂₆H₂₀F₂O₄, monoclinic, *P*₂₁/*n* (no. 14), *a* = 10.3707(2) Å, *b* = 12.0232(2) Å, *c* = 15.7744(3) Å, β = 90.907(1)°, *V* = 1966.65(6) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0371, *wR*_{ref}(*F*²) = 0.1013, *T* = 193.15 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was prepared *via* Zn-mediated reductive coupling reaction [6] of 1,8-bis(2-fluorobenzoyl)-2,7-dimeth-

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.35 × 0.20 × 0.10 mm
Wavelength:	Cu K α radiation (1.54187 Å)
μ :	0.93 mm ⁻¹
Diffractometer, scan mode:	Rigaku R-Axis RAPID, ω
$\theta_{\max}$, completeness:	68.2°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	36,085, 3566, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3380
$N(\text{param})_{\text{refined}}$:	306
Programs:	Rigaku [1, 2], SHELX [3, 4], ORTEP-III [5]

oxynaphthalene. The starting material was synthesized by reference to the literature [7]. In a 10 mL two-necked round-bottomed flask, 1,8-bis(2-fluorobenzoyl)-2,7-dimethoxy-naphthalene (86 mg, 0.2 mmol), zinc (78 mg, 1.2 mmol), zinc chloride (27 mg, 0.2 mmol) and DMAc (0.4 mL) were stirred at 373 K under nitrogen atmosphere. After stirring for 4 h, the reaction mixture was poured into water (30 mL). The resulting aqueous solution was extracted with chloroform (20 mL × three times). The combined organic extracts were washed with 2 M HCl aq (20 mL × three times) and brine (20 mL × three times) successively. The organic layer thus obtained was dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to give a cake. Then the cake was dissolved in chloroform (2 mL) and the solution was added drop-wisely to hexane (200 mL) for reprecipitation. The precipitates were collected by suction filtration (quant.). Colorless block crystals of title compound were obtained by crystallization from ethyl acetate (68% yield). **¹H NMR** δ (300 MHz, CDCl₃): 8.09 (1H, dddd, J = 8.1, 8.1, 2.4 and 2.4 Hz), 7.88 (d, 1H, J = 9.0 Hz), 7.77 (d, 1H, J = 8.7 Hz), 7.29 (d, 1H, J = 9.0 Hz), 7.14 (d, 1H, J = 8.7 Hz), 7.05 (ddd, 1H, J = 7.8, 7.8 and 1.5 Hz), 7.02–6.88 (m, 3H), 6.76 (ddd, 1H, J = 7.8, 7.8 and 1.5 Hz), 6.59 (ddd, 1H, J = 1, 12.0 and 0.9 Hz), 6.25 (ddd, 1H, J = 11.4, 7.8 and 0.9 Hz), 4.48 (s, 1H), 4.31 (d, 1H, J = 6.6 Hz), 3.90 (s, 3H), 3.66 (s, 3H) ppm; **¹³C NMR** δ (75 MHz, CDCl₃): 160.79 ($J_{\text{C-F}}$ = 247 Hz), 158.67 ($J_{\text{C-F}}$ = 246 Hz), 153.53, 153.09, 139.44 (pseudo s, $J_{\text{C-F}}$ = 2.9 Hz), 130.73 ($J_{\text{C-F}}$ = 10.1 Hz), 130.66, 129.43 ($J_{\text{C-F}}$ = 8.6 Hz), 128.73 ($J_{\text{C-F}}$ = 7.9 Hz), 128.34, 128.02, 127.94 ($J_{\text{C-F}}$ = 12.2 Hz), 127.32 ($J_{\text{C-F}}$ = 7.2 Hz), 127.16, 123.76, 123.00 ($J_{\text{C-F}}$ = 2.8 Hz), 122.53 ($J_{\text{C-F}}$ = 2.8 Hz), 122.17, 115.17 ($J_{\text{C-F}}$ = 23.0 Hz), 114.43, 114.10 ($J_{\text{C-F}}$ = 23.0 Hz), 113.61, 89.95 (pseudo s), 85.66 ($J_{\text{C-F}}$ = 2.85 Hz), 56.56, 56.16 ppm. **IR** (KBr): 3505 (O–H), 3464 (O–H), 1630 (Ar), 1581 (Ar), 1504 (Ar), 1485, 1225, 1040 cm⁻¹. **HRMS** (m/z): $[M+H-H_2O]^+$ calcd. for C₂₆H₁₉F₂O₃, 417.1302, found, 417.1318. **m.p.** = 450–451 K.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.98369 (13)	0.31411 (11)	0.17894 (8)	0.0258 (3)
C2	1.07530 (13)	0.39373 (12)	0.19528 (9)	0.0291 (3)
C3	1.20809 (14)	0.36570 (12)	0.18799 (9)	0.0325 (3)
H3	1.2716	0.4212	0.1985	0.039*
C4	1.24645 (13)	0.26042 (13)	0.16621 (9)	0.0322 (3)
H4	1.3357	0.2446	0.1607	0.039*
C5	1.17750 (13)	0.06201 (12)	0.13210 (9)	0.0327 (3)
H5	1.2636	0.0361	0.1276	0.039*
C6	1.07676 (14)	−0.01071 (12)	0.11942 (9)	0.0320 (3)
H6	1.0950	−0.0861	0.1063	0.038*
C7	0.94611 (13)	0.02378 (11)	0.12541 (9)	0.0277 (3)
C8	0.92073 (12)	0.13242 (11)	0.14637 (8)	0.0254 (3)
C9	1.02378 (13)	0.20590 (11)	0.15880 (8)	0.0257 (3)
C10	1.15442 (13)	0.17505 (12)	0.15186 (9)	0.0286 (3)
C11	0.83781 (13)	0.31780 (11)	0.18745 (8)	0.0262 (3)
C12	0.76872 (13)	0.40893 (11)	0.13776 (9)	0.0293 (3)
C13 ^a	0.63866 (14)	0.43100 (13)	0.14949 (10)	0.0368 (3)
H13	0.5923	0.3858	0.1879	0.044*
C14	0.57381 (18)	0.51553 (15)	0.10789 (13)	0.0512 (5)
H14	0.4852	0.5288	0.1183	0.061*
C15	0.6396 (2)	0.58053 (15)	0.05091 (13)	0.0562 (5)
H15	0.5963	0.6391	0.0218	0.067*
C16	0.76816 (19)	0.56041 (14)	0.03620 (11)	0.0473 (4)
H16	0.8133	0.6047	−0.0034	0.057*
C17 ^b	0.83134 (16)	0.47555 (12)	0.07931 (10)	0.0355 (3)
H17	0.9200	0.4625	0.0686	0.043*
C18	0.79264 (12)	0.19123 (11)	0.16029 (8)	0.0256 (3)
C19	0.70565 (12)	0.18631 (11)	0.08137 (9)	0.0254 (3)
C20	0.58102 (13)	0.14344 (12)	0.08438 (10)	0.0318 (3)
H20	0.5483	0.1188	0.1371	0.038*
C21	0.50367 (15)	0.13599 (13)	0.01195 (11)	0.0380 (4)
H21	0.4187	0.1070	0.0158	0.046*
C22	0.54886 (15)	0.17018 (13)	−0.06560 (10)	0.0392 (4)
H22	0.4957	0.1643	−0.1150	0.047*
C23	0.67255 (15)	0.21313 (12)	−0.07087 (9)	0.0343 (3)
H23	0.7052	0.2375	−0.1236	0.041*
C24	0.74705 (13)	0.21969 (11)	0.00204 (9)	0.0277 (3)
C25	1.09837 (18)	0.58978 (13)	0.18453 (12)	0.0463 (4)
H25A	1.0631	0.6587	0.2079	0.056*
H25B	1.1911	0.5862	0.1970	0.056*
H25C	1.0839	0.5885	0.1230	0.056*
C26	0.86957 (15)	−0.15402 (12)	0.07840 (10)	0.0342 (3)
H26A	0.7886	−0.1954	0.0721	0.041*
H26B	0.9098	−0.1464	0.0229	0.041*
H26C	0.9280	−0.1942	0.1170	0.041*
F1A ^b	0.57062 (9)	0.36665 (9)	0.20276 (7)	0.0457 (3)
F1B ^a	0.9303 (15)	0.4543 (14)	0.0459 (9)	0.043 (4)
F2	0.86876 (8)	0.26034 (7)	−0.00543 (5)	0.0346 (2)
O1	0.81215 (10)	0.32802 (10)	0.27618 (6)	0.0338 (2)
H1	0.783 (2)	0.3883 (19)	0.2849 (14)	0.060 (7)*
O2	0.72549 (10)	0.14048 (9)	0.22742 (7)	0.0334 (2)
H2	0.746 (2)	0.1767 (19)	0.2702 (15)	0.060 (7)*

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O3	1.03595 (10)	0.49682 (8)	0.22181 (7)	0.0367 (3)
O4	0.84373 (9)	−0.04593 (8)	0.11230 (7)	0.0321 (2)

^aOccupancy: 0.06, ^bOccupancy: 0.94.

Experimental details

All H atoms were found in a difference map and were subsequently refined as riding atoms, with C–H = 0.95 (aromatic) and 0.98 (methyl) Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Comment

Weak interactions such as non-classical hydrogen bond [8–11] are ordinarily latent, however, crystals of non-coplanarly accumulated aromatic rings compounds can expectingly pull out weak interactions by depressing $\pi \cdots \pi$ stacking. Such a skeleton is embodied in title pinacol, which is reductively coupling product of *peri*-aroylnaphthalene compounds [12–17]. In the title molecular structure, two 2-fluorophenyl groups are oriented in a same direction against the acenaphthene ring (Figure). The cyclopentane moiety (C1–C9–C8–C18–C11 ring) and the naphthalene moiety (C1–C10 ring) of the acenaphthene ring are almost coplanar (dihedral angle = 2.06°; C1–C11–C18–C8 = 3.78(12)°). The dihedral angles between fluorobenzene rings and the naphthalene ring are 55.62° [C12–C17 ring; C1–C11–C12–C13 = −170.79(13)°] and 86.70° [C19–C24 ring; C8–C18–C19–C20 = 124.74(13)°], respectively. The dihedral angle between the best planes of the two fluorobenzene rings is 51.34(8)°. Three kinds of intramolecular non-covalent bonding interactions are observed: O–H $\cdots$ O classical hydrogen bond between hydroxy groups at 1,2-positions [1.95(2) Å, H2 $\cdots$ O1], C–H $\cdots$ O non-classical hydrogen bond between H2O atom of 2-fluorophenyl moiety and oxygen atom of hydroxy group (2.32 Å, H2O $\cdots$ O2), and C–F $\cdots$ π interaction between F2 atom and cyclopentane moiety [2.7602(10) Å, F2 $\cdots$ Cg1; Cg1 = C1–C9–C8–C18–C11 ring]. On the other 2-fluorophenyl group, the fluorine atom is disordered over two positions with site occupancies of 0.94 and 0.06 [F1A and F1B]. Therefore, the title compound is postulated as a mixture of two components, *i.e.*, *endo-exo* (F2 and F1A/H17; major component) and *endo-endo* (F2 and F1B/H13; minor one) types. In the crystal packing, intermolecular classical hydrogen bond between hydroxy and methoxy groups links molecules into two-fold helical molecular aggregation along the *b*-axis [2.25(2) Å, H1 $\cdots$ O4; symmetry code: 3/2−*x*, 1/2+*y*, 1/2−*z*]. The two-fold helical

molecular aggregations are further gathered by two bidirectional forces: the C–H $\cdots$ π non-classical hydrogen bond between a methoxy group and the naphthalene ring along *c*-axis [2.66 Å, H26B $\cdots$ Cg3; Cg3 = C5–C10 ring; symmetry code: 2−*x*, −*y*, −*z*] and a C–H $\cdots$ O non-classical hydrogen bond between the H22 atom of the 2-fluorophenyl group and the hydroxy oxygen along *a*-axis [2.54 Å, H22 $\cdots$ O1; symmetry code: −1/2+*x*, 1/2−*y*, −1/2+*z*]. The hydroxy group (O2–H) that shares its hydrogen atom with the other hydroxy group (O1–H) also makes a non-classical hydrogen bond with the hydrogen atom (H–C20) forming a warped six–five–five fused tricyclic structure, at the end of which the fluorine atom (F2) occupying the opposite *o*-position intramolecularly interacts with the cyclopentane moiety. On the other phenyl group, the *o*-positioned hydrogen and fluorine atoms are free from effective interactions, which induces comparably stable two components as displayed in disorder of two atoms.

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