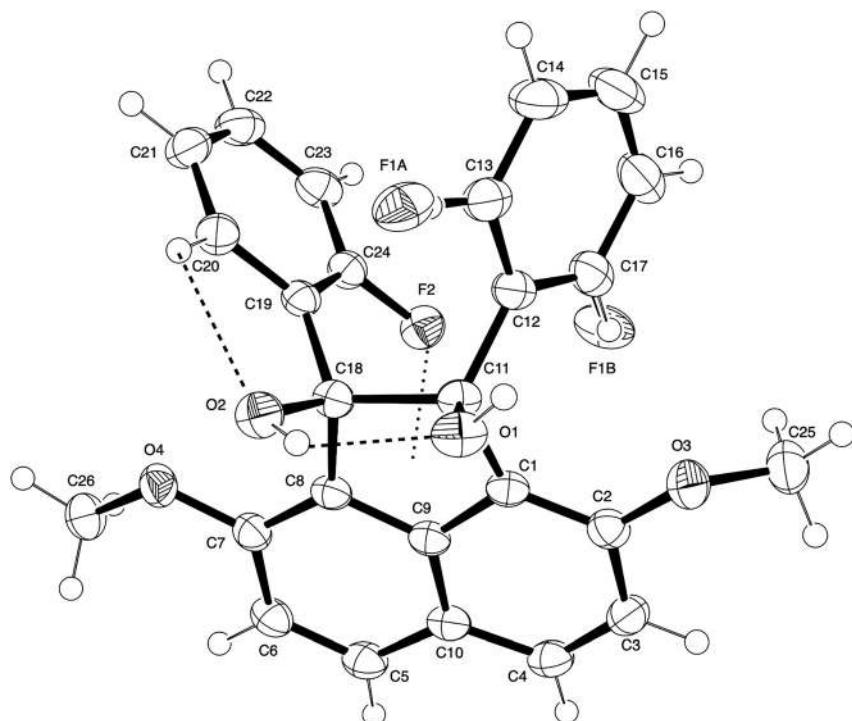


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The crystal structure of ($1R^*, 2S^*$)-1,2-bis(2-fluorophenyl)-3,8-dimethoxyacenaphthene-1,2-diol, $C_{26}H_{20}F_2O_4$



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Abstract

$C_{26}H_{20}F_2O_4$, monoclinic, $P2_1/n$ (no. 14), $a = 10.3707(2)$ Å, $b = 12.0232(2)$ Å, $c = 15.7744(3)$ Å, $\beta = 90.907(1)^\circ$, $V = 1966.65(6)$ Å 3 , $Z = 4$, $R_{gt}(F) = 0.0371$, $wR_{ref}(F^2) = 0.1013$, $T = 193.15$ 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 |
| θ_{max} , completeness: | 68.2°, 99% |
| $N(hkl)$, measured, $N(hkl)$, unique, R_{int} : | 36,085, 3566, 0.022 |
| Criterion for I_{obs} , $N(hkl)$, gt: | $I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3380 |
| $N(\text{param})$, 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_{C-F} = 247 Hz), 158.67 (J_{C-F} = 246 Hz), 153.53, 153.09, 139.44 (pseudo s, J_{C-F} = 2.9 Hz), 130.73 (J_{C-F} = 10.1 Hz), 130.66, 129.43 (J_{C-F} = 8.6 Hz), 128.73 (J_{C-F} = 7.9 Hz), 128.34, 128.02, 127.94 (J_{C-F} = 12.2 Hz), 127.32 (J_{C-F} = 7.2 Hz), 127.16, 123.76, 123.00 (J_{C-F} = 2.8 Hz), 122.53 (J_{C-F} = 2.8 Hz), 122.17, 115.17 (J_{C-F} = 23.0 Hz), 114.43, 114.10 (J_{C-F} = 23.0 Hz), 113.61, 89.95 (pseudo s), 85.66 (J_{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–H₂O]⁺ 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 | x | y | z | U_{iso}^* / U_{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 | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|-------------|----------------------------------|
| 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*-arylnaphthalene 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···O classical hydrogen bond between hydroxy groups at 1,2-positions [1.95(2) Å, H2···O1], C–H···O non-classical hydrogen bond between H20 atom of 2-fluorophenyl moiety and oxygen atom of hydroxy group (2.32 Å, H20···O2), and C–F···π interaction between F2 atom and cyclopentane moiety [2.7602(10) Å, F2···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···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···π non-classical hydrogen bond between a methoxy group and the naphthalene ring along *c*-axis [2.66 Å, H26B···Cg3; Cg3 = C5–C10 ring; symmetry code: 2–x, -y, -z] and a C–H···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···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-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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