

# Crystal structure of 1-(4-hydroxybenzoyl)-2,7-dimethoxynaphthalene: Contribution of classical and non-classical hydrogen bonding interactions to the molecular packing structure

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## ARTICLE INFORMATION



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## ABSTRACT

Crystal structure of 1-(4-hydroxybenzoyl)-2,7-dimethoxynaphthalene,  $C_{19}O_4H_{16}$ , is reported from the viewpoint of characteristics in the helical alignments and difference compared to the crystal structure of a structural isomeric compound. The asymmetric unit of title compound contains two conformers A and B. Furthermore, the molecules in crystal exhibit atropisomerism brought about by molecular stereogenic axis of carbon-carbon bond between the carbonyl moiety and the naphthalene ring. Therefore, a pair of *R*- and *S*-enantiomeric molecules exists for each conformer. The two pairs of the enantiomeric molecules are related by two-fold helical axis in the asymmetric unit of  $P2_1/c$  space group, exhibiting the number of molecules is eight,  $Z = 8$ . Single molecular structure of title compound shows non-coplanarly accumulated aromatic-rings structure. The molecular packing structure is mainly stabilized non-classical hydrogen bonds involving C-H...O hydrogen bonds and C-H... $\pi$  ones, however O-H...O=C classical hydrogen bonds are solely formed between same configured conformers. Comparison with the spatial alignment of an isomeric homologue, 2-hydroxy-1-(4-methoxybenzoyl)-7-methoxynaphthalene, has clarified that substitution position of hydroxy group determines not only direction of classical hydrogen bonds but also total feature of molecular packing, *i.e.*, the homologous compound, which has hydroxy group at 2-position of naphthalene core forms intramolecular O-H...O=C classical hydrogen bond, and O-H...OMe classical hydrogen bonds between opposite enantiomeric isomers. The presence/absence and direction of the predominantly strong classical hydrogen bonds govern balance of interactions of other less effective classical and non-classical hydrogen bonds in molecular packing. In homologous compound, each of non-classical hydrogen bonds between same signed enantiomeric isomers and those between opposite enantiomeric isomers demonstrates almost same distances. In title compound, both types of non-classical hydrogen bonds formed by conformer A are imbalanced. The imbalanced non-classical hydrogen bonds are adjusted and reinforced by non-classical hydrogen bonds between conformers A and B.

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## 1. Introduction

Non-coplanarly accumulated-aromatic-rings containing compounds such as aromatic ring assembly of binaphthyl and biphenyl have received much attention from wide-range of organic chemists and material chemists as useful molecular building block [1-4]. The spatial organizations of aromatic rings in these molecules are fixed as non-coplanar accumulation mode leading to expression of enantioselectivity and regioselectivity in organic reaction. On the other hand, the aromatic ketone compounds bearing some restriction against structural alteration also have non-coplanar alignment of aromatic rings with relatively loose conformational fixation of substituents. Recently, the authors have found highly efficient diarylation at *peri*(1,8)-positions of 2,7-dialkoxy-naphthalene compounds [5,6]. *peri*-Aroylated naphthalene compounds thus

obtained are proved to have non-coplanarly accumulated aromatic-rings-structure in crystal, *i.e.*, the aryl groups are twistedly situated to the naphthalene ring core in a perpendicular fashion [7-9]. Besides, the two aryl groups are ordinarily oriented in an opposite direction with a few exceptional compounds bearing unidirectionally-aligned aryl groups [10,11]. The non-coplanarly congested aromatic rings spatial organization makes the authors imagine that formation of strong  $\pi$ ... $\pi$  stacking interactions should be restricted. Indeed, molecules of *peri*-aroylnaphthalene compounds are accumulated by weak hydrogen bonding interactions, mainly of non-classical hydrogen bonding interaction category in crystal. In the molecular packing of *peri*-aroylnaphthalene compounds, four kinds of non-covalent-bonding interactions, ( $sp^2$ )C-H...O=C hydrogen bond, ( $sp^3$ )C-H...O hydrogen bond, C-H... $\pi$  hydrogen-bonding interaction, and  $\pi$ ... $\pi$  stacking are

**Table 1.** Crystallographic data and structure refinement parameters.

|   |  |
|---|--|
| <i>Crystal data</i>   |  |
| Chemical formula  | C <sub>19</sub> H <sub>16</sub> O <sub>4</sub> |
| M <sub>r</sub>  | 308.32   |
| Crystal shape, colour   | Platelet, colourless                           |
| Crystal system, space group                                       | Monoclinic, P2 <sub>1</sub> /c                 |
| Temperature (K)   | 193.0  |
| a (Å)   | 7.88320 (10)                                   |
| b (Å)   | 15.9187 (3)                                    |
| c (Å)   | 24.6606 (4)                                    |
| β (°)   | 92.6120 (10)                                   |
| V (Å <sup>3</sup> )   | 3091.45 (9)                                    |
| Z   | 8  |
| Radiation type  | CuKα   |
| μ (mm <sup>-1</sup> )   | 0.76   |
| Crystal size (mm)   | 0.50 × 0.20 × 0.10                             |
| <i>Data collection</i>  |  |
| Diffractometer  | Rigaku R-AXIS RAPID diffractometer             |
| Absorption correction   | Numerical NUMABS                               |
| T <sub>min</sub> , T <sub>max</sub>                               | 0.703, 0.928                                   |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 56413, 5667, 4390                              |
| R <sub>int</sub>  | 0.049  |
| (sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )                       | 0.602  |
| <i>Refinement</i>   |  |
| R[F <sup>2</sup> > 2σ(F <sup>2</sup> )], wR(F <sub>2</sub> ), S   | 0.043, 0.130, 1.02                             |
| No. of reflections  | 5667   |
| No. of parameters   | 422  |
| H-atom treatment  | H-atom parameters constrained                  |
| Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )        | 0.18, -0.17                                    |
| CCDC no.  | 1520592  |

observed in decreasing order of frequency [12]. In solution, various conformations of aroyl groups in *peri*-aroylnaphthalene compounds are formed around the carbon-carbon bond between the carbonyl group and the naphthalene ring [13]. In this regard, the expected flexibility of the aromatic ketone compound probably shows great variation in single molecular and packing structures in the crystal. Such a situation offers a good opportunity to reveal the hitherto unclarified interactions that determine the spatial organization of aromatic rings accumulated molecules in the crystalline state. This article reports the synthesis and crystal structure of the 1-(4-hydroxybenzoyl)-2,7-dimethoxynaphthalene. Furthermore, the correlation among the single molecular structure, the non-covalent bonding interactions, and the molecular packing is discussed through comparison of the structural isomer, 2-hydroxy-1-(4-methoxybenzoyl)-7-methoxynaphthalene [14].

## 2. Experimental

### 2.1. Materials and methods

All reagents were of commercial quality and were used as received. Solvents were dried and purified using standard procedures [15]. Synthetic methods and spectral data for 2-hydroxy-1-(4-methoxybenzoyl)-7-methoxynaphthalene [14] and 1-(4-fluorobenzoyl)-2,7-dimethoxynaphthalene [16] have been reported in literatures.

### 2.2. Measurements

<sup>1</sup>H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (300 MHz) or a JEOL ECX400 spectrometer (400 MHz). Chemical shifts are expressed in ppm relative to internal standard of Me<sub>4</sub>Si (δ, 0.00). <sup>13</sup>C NMR spectra were recorded on a JEOL ECX400 spectrometer (100 MHz). Chemical shifts are expressed in ppm relative to internal standard of CDCl<sub>3</sub> (δ, 77.0). IR spectra were recorded on a JASCO FT/IR-4100 spectrometer (KBr tablet). Elemental analyses were performed on a Yanaco CHN CORDER MT-5 analyzer.

### 2.3. X-ray crystallography

For the crystal structure determination, the single-crystal of title compound was used for data collection on a four-circle Rigaku RAXIS RAPID diffractometer (equipped with a two-dimensional area IP detector). The graphite-mono-chromated CuKα radiation (λ = 1.54187 Å) was used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with  $F^2 > 2\theta(F^2)$ .

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms could be located in difference Fourier maps, but were subsequently refined in optimized positions as riding atoms, with C-H = 0.95 (aromatic) and 0.98 (methyl) and with  $U_{iso}(H) = 1.2 U_{eq}(C)$ . For data collection: *PROCESS-AUTO* [17]; cell refinement: *PROCESS-AUTO* [17]; data reduction: *CrystalStructure* [18]; program(s) used to solve structure: *SIR2004* [19]; program(s) used to refine structure: *SHELXL97* [20]; molecular graphics: *ORTEP III* [21]. The hydrogen bond geometries of title compound are listed in Table 2.

### 2.4. Synthesis of title compound

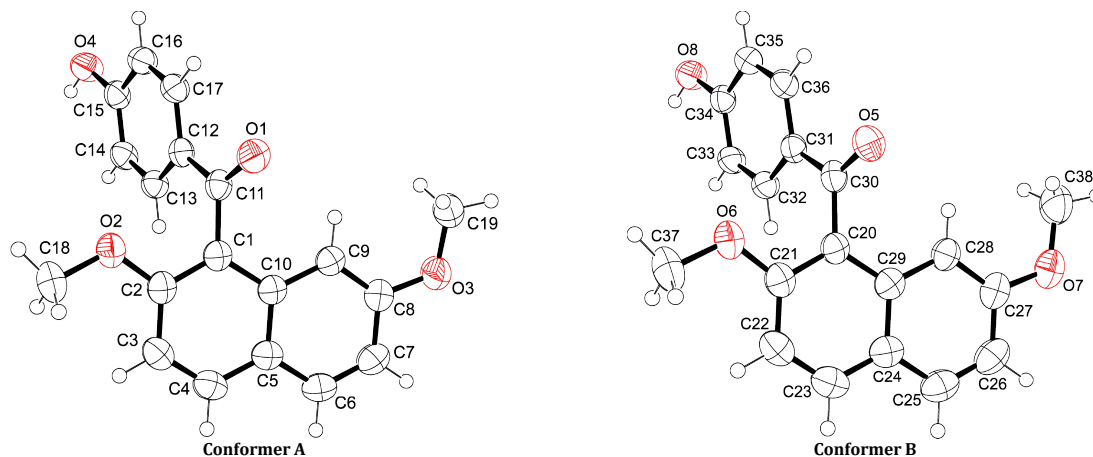
To a 10 mL flask, 1-(4-fluorobenzoyl)-2,7-dimethoxynaphthalene (0.20 mmol, 62 mg), sodium hydroxide (1.0 mmol, 40 mg), dimethyl sulfoxide (0.38 mL), and water (0.13 mL) were placed and stirred at 120 °C for 12 h. After the reaction, the mixture was poured into ice-cooled water. The aqueous solution was acidified with hydrochloric acid to give cake. Slightly yellow precipitates thus obtained were collected with suction filtration. The crude product was purified by recrystallization from ethanol.

*1-(4-Hydroxybenzoyl)-2,7-dimethoxynaphthalene*: Color: Colourless. Yield: 65%. M.p.: 180-182 °C. FT-IR (KBr, ν, cm<sup>-1</sup>): 3367 (OH) (br, alcohol), 1642 (C=O) (ketone), 1626 (Ar), 1602 (Ar), 1575 (Ar), 1514 (Ar), 1277 (Ar-O-CH<sub>3</sub>), 1251 (ArC-OH), 1087 (ArC-O-CH<sub>3</sub>), 1049 (ArC-O-CH<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ, ppm): 3.69 (s, 3H, OCH<sub>3</sub>), 3.79 (s, 3H, OCH<sub>3</sub>), 6.40 (br, 1H, OH), 6.74 (d, *J* = 2.1 Hz, 1H, naphthalene-H), 6.80 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.00 (dd, *J* = 2.4, 9.0 Hz, 1H, naphthalene-H),

**Table 2.** Hydrogen bond geometry (Å, °).

| Hydrogen bond                | D-H  | H...A | D...A      | D—H...A |
|------------------------------|------|-------|------------|---------|
| O4-H39...O1 <sup>i</sup>     | 0.84 | 1.94  | 2.7661(15) | 170     |
| O8-H40...O5 <sup>i</sup>     | 0.84 | 1.92  | 2.7402(17) | 165     |
| C14-H14...O1 <sup>i</sup>    | 0.95 | 2.44  | 3.1402(18) | 131     |
| C7-H7...O4 <sup>ii</sup>     | 0.95 | 2.62  | 3.382(2)   | 138     |
| C33-H33...O5 <sup>i</sup>    | 0.95 | 2.50  | 3.1650(19) | 127     |
| C35-H35...O3 <sup>iii</sup>  | 0.95 | 2.57  | 3.4710(19) | 159     |
| C37-H37...O1 <sup>iv</sup>   | 0.98 | 2.58  | 3.487(2)   | 154     |
| C18-H18B...Cg <sup>v</sup>   | 0.98 | 2.71  | 3.3574(18) | 124     |
| C26-H26...Cg <sup>vi</sup>   | 0.95 | 2.83  | 3.7463(18) | 163     |
| C4-H4...Cg <sup>i</sup>      | 0.95 | 2.90  | 3.4072(18) | 115     |
| C19-H19B...Cg <sup>vii</sup> | 0.98 | 2.80  | 3.7336(18) | 159     |

Symmetry codes: (i)  $-1+x, y, z$ ; (ii)  $-x, -1/2+y, 1/2-z$ ; (iii)  $x, 1/2-y, 1/2+z$ ; (iv)  $1-x, 1-y, 1-z$ ; (v)  $-x, 1-y, 1-z$ ; (vi)  $1-x, -1/2+y, 1/2-z$ ; (vii)  $1-x, 1/2+y, 1/2-z$ .

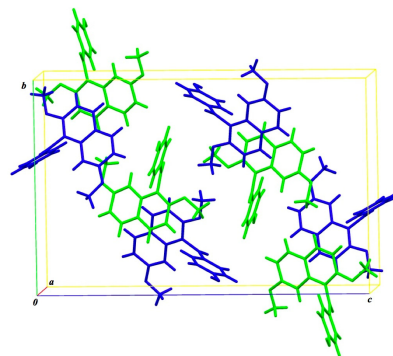
**Figure 1.** Molecular structures of conformers A and B with displacement ellipsoids at 50% probability.

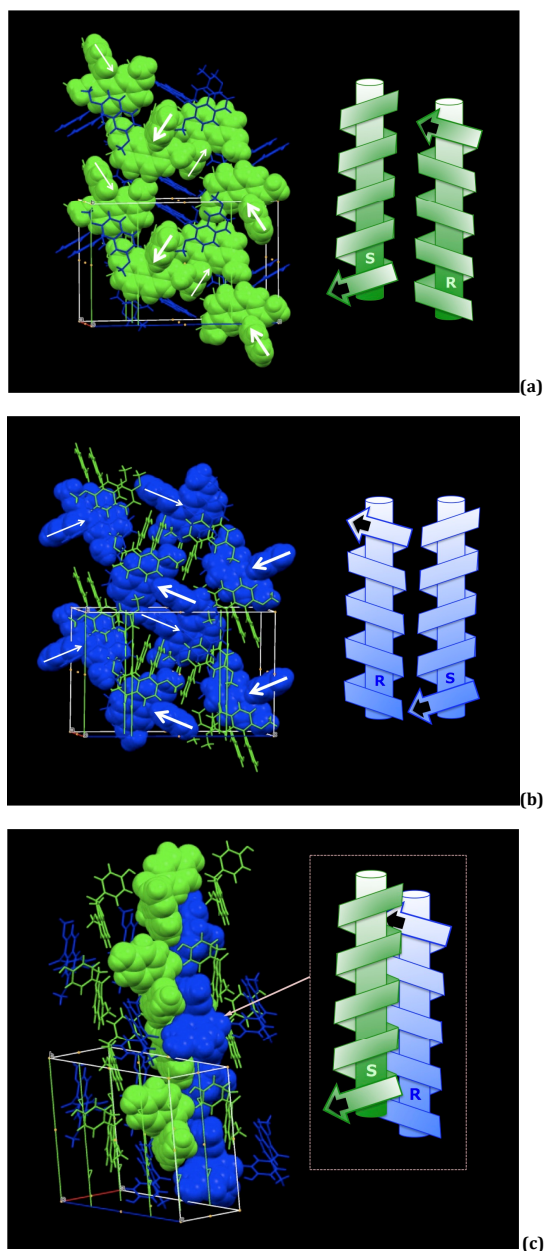
7.14 (d,  $J = 9.0$  Hz, 1H, naphthalene-H), 7.70 (d,  $J = 9.0$  Hz, 1H, naphthalene-H), 7.75 (d,  $J = 8.7$  Hz, 2H, Ar-H), 7.83 (d,  $J = 9.0$  Hz, 1H, naphthalene-H).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 194.863 (1C, C=O), 162.613 (1C, Ar-C-OMe), 158.114 (1C, Ar-C-OMe), 154.133 (1C, Ar-C-OH), 132.210 (1C, Ar-C), 131.691 (1C, Ar-C), 130.479 (2C, Ar-C), 129.902 (1C, Ar-C), 129.111 (1C, Ar-C), 123.804 (1C, Ar-C), 121.537 (1C, Ar-C), 116.098 (2C, Ar-C), 115.488 (1C, Ar-C), 110.856 (1C, Ar-C), 101.955 (1C, Ar-C), 56.074 (1C, OCH<sub>3</sub>), 54.838 (1C, OCH<sub>3</sub>). Anal. calcd. for C<sub>19</sub>H<sub>16</sub>O<sub>4</sub>: C, 74.01; H, 5.23. Found: C, 74.10; H, 5.21%.

### 3. Results and discussion

The authors report crystal structure of title compound, 1-(4-hydroxybenzoyl)-2,7-dimethoxynaphthalene especially focusing on helical alignments of the molecules with the structural difference of two conformers both in single molecular organization and in accumulation feature. In title compound molecule, the 4-hydroxybenzoyl group is non-coplanarly situated against the 2,7-dimethoxynaphthalene ring core. In addition, there are two independent molecular conformational isomers for title compound, conformers A and B (Figure 1). Furthermore, the carbon-carbon bond between the carbonyl moiety and the naphthalene ring acts as a stereogenic axis affording atropisomerism to the molecule. Both conformers have *R*- and *S*-enantiomeric forms. Moreover, the molecules are aligned forming 2<sub>1</sub> helical structure along *b*-axis. Therefore, two pairs of *R*- and *S*-enantiomeric molecules exist for both conformers in the asymmetric units, which are positioned in 2<sub>1</sub> helical crystal circumference, giving  $Z = 8$  (Figure 2). Two conformers show rather small difference in spatial organization of single molecular structure. Interplanar angles between benzene ring and naphthalene ring for conformers A and B are 69.86° (O=C-C-C torsion angle = -63.59°) and 72.12° (O=C-C-C torsion angle = 67.77°), respectively. In mole-

cular packing of title compound, *R*- and *S*-enantiomeric isomers for each conformer form a molecular assembly with a two-fold screw mode along *b*-axis. The 2<sub>1</sub> helical assembly can be differentiated as right-handedness or left-handedness, and also as upwardness or downwardness [22-25]. Conformers A and B show same correlation between the absolute configuration of the molecule and the handedness and the orientation of the 2<sub>1</sub> helical assembly (Figure 3; conformer A: green-colored; conformer B: blue-colored). *S*(*R*)-Enantiomeric molecules form right (left)-handed and downward (upward) 2<sub>1</sub> helical assembly. The right-handed 2<sub>1</sub> helical assemblies of conformer A are alternately arranged with the left-handed ones in an opposite orientation along *c*-axis (Figure 4). Furthermore, the right(left)-handed 2<sub>1</sub> helical assemblies of conformer A are alternately stacked with left(right)-handed ones of conformer B in an opposite orientation along *a*-axis (Figure 4).

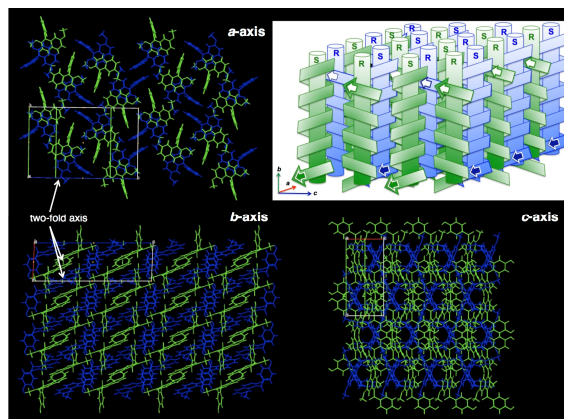
**Figure 2.** Molecular packing structure of title compound. Conformer A and B are expressed as green and blue, respectively.



**Figure 3.** Correlation between absolute configuration of molecule and the handedness and the orientation of  $2_1$  helical assemblies in conformer A (a) and conformer B (b), and arrangements of  $2_1$  helical assemblies of two conformers (c).

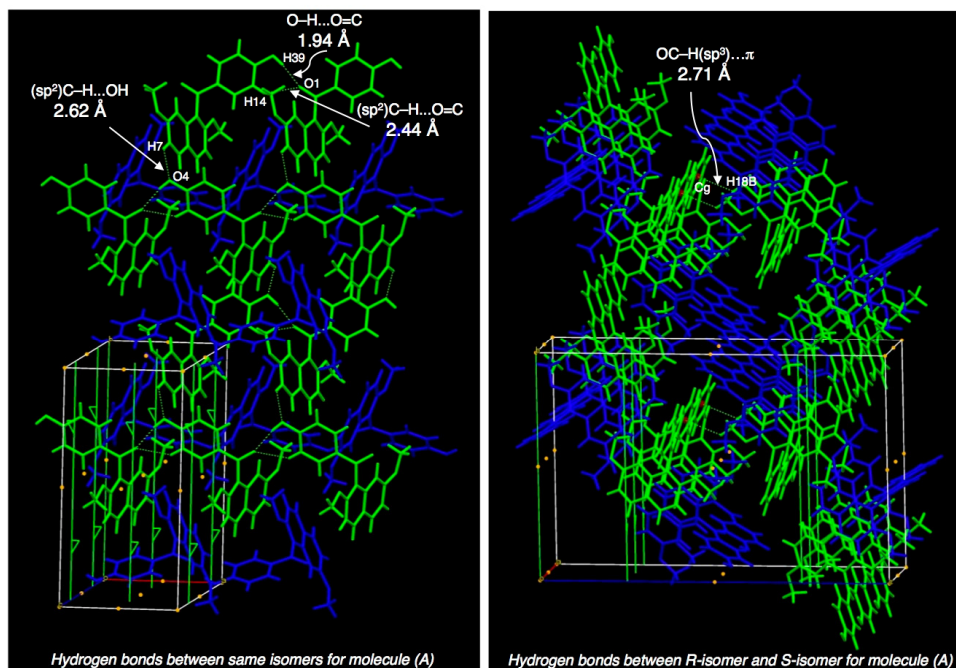
For conformer A of title compound, there are no effective interactions along the direction of  $b$ -axis among  $S(R)$ -enantiomeric molecules in a right(left)-handed  $2_1$  helical assembly. The right(left)-handed  $2_1$  helical assemblies composed of  $S(R)$ -enantiomeric molecules of conformer A are connected to each other *via* O-H...O=C classical hydrogen bonds [O4-H39...O1 = 1.94 Å] and two kinds of non-classical hydrogen bonds, {benzoyl}(sp<sup>2</sup>)C-H...O=C [C14-H14...O1 = 2.44 Å] and {naph}(sp<sup>2</sup>)C-H...OH hydrogen bonds [C7-H7...O4 = 2.62 Å] along  $a$ -axis (Figure 5, left). The right-handed  $2_1$  helical assemblies composed of  $S$ -enantiomeric molecules of conformer A are linked with the left-handed one composed of  $R$ -enantiomeric molecules of conformer A by {naph}OC-H(sp<sup>3</sup>)...π non-classical hydrogen bonds (C18-H18B...Cg = 2.71 Å) along  $c$ -axis (Figure 5, right). In the case of conformer B,  $R(S)$ -enantiomeric molecules forming left(right)-handed  $2_1$

helical assembly along  $b$ -axis have no effective non-covalent bonding interactions along the direction of  $b$ -axis to each other as observed in the  $2_1$  helical structure composed of conformer A. The left(right)-handed  $2_1$  helical assemblies composed of  $R(S)$ -enantiomeric molecules of conformer B are connected to each other along  $a$ -axis by O-H...O=C classical hydrogen bonds [O8-H40...O5 = 1.92 Å] and {benzoyl}(sp<sup>2</sup>)C-H...O=C non-classical hydrogen bond [C33-H33...O5 = 2.50 Å] as same as the interactions among conformers A (Figure 6). However, there are no effective non-covalent bonding interactions between the left-handed  $2_1$  helical assemblies and the right-handed  $2_1$  helical ones along  $c$ -axis, in contrast to the helical structure of conformer A. This means that conformers B form effective hydrogen bonding interactions mainly with conformers A. The  $S(R)$ -enantiomeric molecules of conformer B are connected to  $S(R)$ -enantiomeric molecules of conformer A in a head-to-tail fashion by two kinds of non-classical hydrogen bonds, {(B)benzoyl}(sp<sup>2</sup>)C-H...OMe(A) and {(B)naph}OC-H(sp<sup>3</sup>)...O=C(A) hydrogen bonds [C35-H35...O3 = 2.57 Å and C37-H37C...O1 = 2.58 Å] along  $c$ -axis (Figure 7, left). The  $R(S)$ -enantiomeric molecules of conformer A are linked to the  $S(R)$ -enantiomeric molecules of conformer A with two types of non-classical C-H...π hydrogen bonds, head-to-tail-typed {(B)naph}(sp<sup>2</sup>)C-H...π {benzoyl(A)} hydrogen bonds [C26-H26...Cg = 2.83 Å], and tail-to-tail-typed {(A)naph}(sp<sup>2</sup>)C-H...π{naph(B)} and {(A)naph}(sp<sup>3</sup>)OC-H...π{naph(B)}[C4-H4...Cg = 2.90 Å and C19-H19B...Cg = 2.80 Å] along  $b$ -axis (Figure 7, right). These results can be interpreted that conformers B are situated to reinforce the molecular alignment of conformer A.

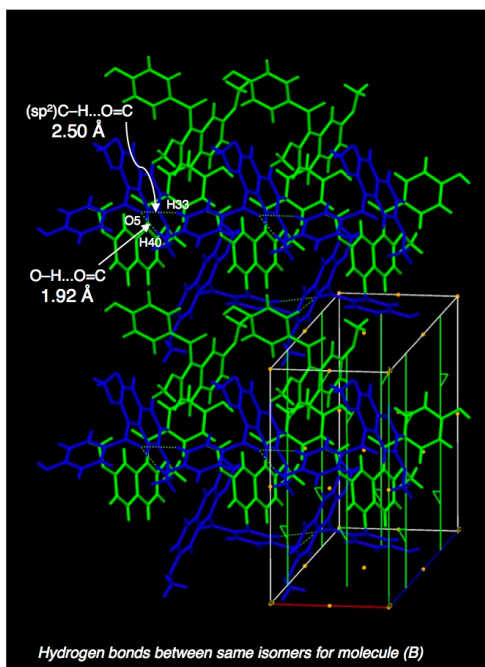


**Figure 4.** Molecular packing structure of title compound viewed down three directions.

Recently, the authors have reported crystal structure of a structural isomer of title compound, 2-hydroxy-1-(4-methoxybenzoyl)-7-methoxynaphthalene (Figure 8) [14]. There is only small difference in molecular structure between title compound and the homologous compound, *i.e.*, position of the hydroxy group. The hydroxy group is situated at  $p$ -position (4-position) of the benzoyl group in title compound, whereas that is attached to 2-position of the naphthalene ring in the homologous compound. The homologous compound has no conformers in the crystal. The intramolecular O-H...O=C hydrogen bonding of the hydroxy group at 2-position of the naphthalene ring to the neighbouring carbonyl group is observed [1.79 Å]. Consequence of this, the dihedral angle between bridged C-(C=O)-C plane and naphthalene ring is smaller than the corresponding dihedral angle of title compound [41.23 ° vs. 64.32 ° (Conformer A) and 67.55 ° (Conformer B)]. In a similar manner to title compound, the homologous molecules form  $2_1$  helical assembly with a two-fold axis along  $b$ -axis in the crystal packing structure.



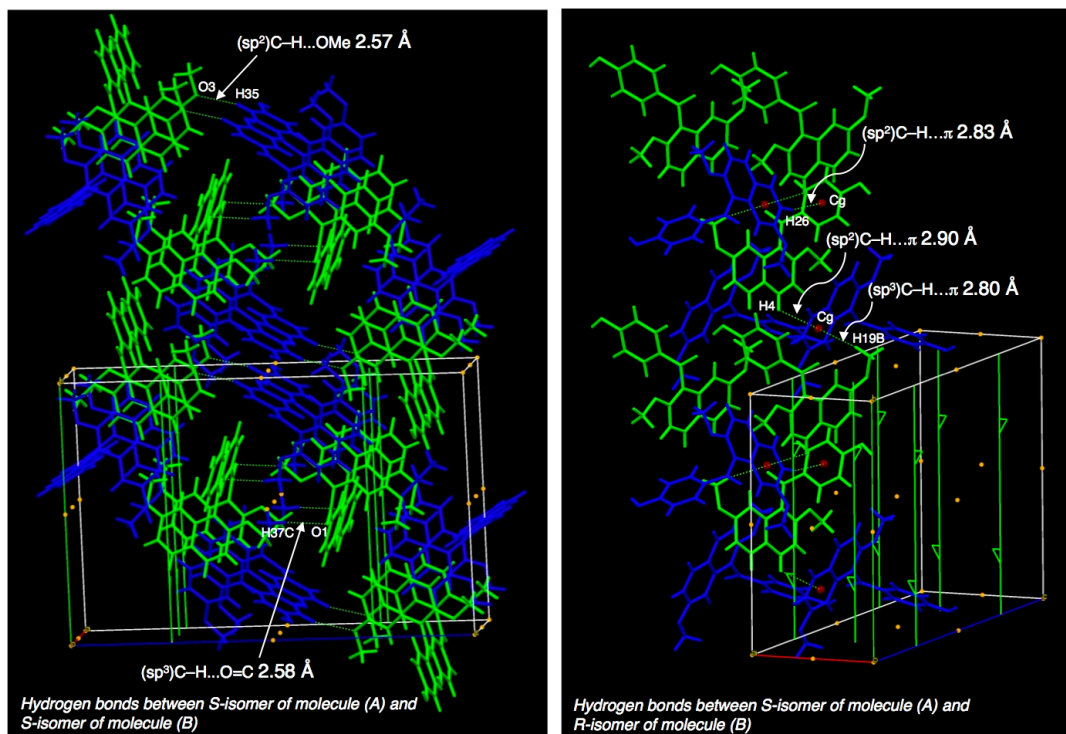
**Figure 5.** Hydrogen bonds of conformers A in crystal of title compound: hydrogen bonds between same enantiomeric molecules (left) and hydrogen bonds between opposite-enantiomeric molecules (right).



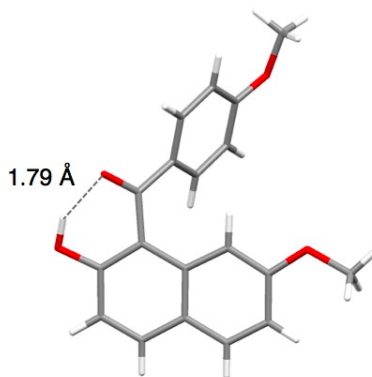
**Figure 6.** Hydrogen bonds of conformers B in crystal of title compound: hydrogen bonds between same enantiomeric molecules.

However, the correlation between the absolute configuration of the molecule and the handedness of the  $2_1$  helical assembly is inversely related to title compound, *i.e.*,  $S(R)$ -enantiomeric molecules form left(right)-handed  $2_1$  helical assembly (Figure 9,  $S$ -enantiomeric isomers and  $R$ -enantiomeric isomers are expressed as pink-colored molecules and pale blue-colored molecules, respectively). Both right-handed and left-handed  $2_1$  helical assemblies are oriented in upward. Left(Right)-handed  $2_1$  helical assemblies are aligned along  $a$ -

axis, and are alternately arranged with right(left)-handed  $2_1$  helical assemblies along  $c$ -axis in same orientation.  $S(R)$ -enantiomeric molecules of the homologous compound are linked to each other through {benzoyl}OC-H( $sp^3$ )... $\pi$ {naph} non-classical hydrogen bond [2.82 Å] forming left(right)-handed  $2_1$  helical assembly along  $b$ -axis (Figure 10, left). The left(right)-handed  $2_1$  helical assemblies aligned along  $a$ -axis are connected to each other by {naph}{ $sp^2$ }C-H... $\pi$ {benzoyl} non-classical hydrogen bonds [2.81 Å] (Figure 10, left).



**Figure 7.** Hydrogen bonds between conformers A and conformers B in crystal of title compound: hydrogen bonds between *S*-enantiomeric molecules of conformer A and *S*-enantiomeric molecules of conformer B (left) and hydrogen bonds between *S*-enantiomeric molecules of conformer A and *R*-enantiomeric molecules of conformer B (right).

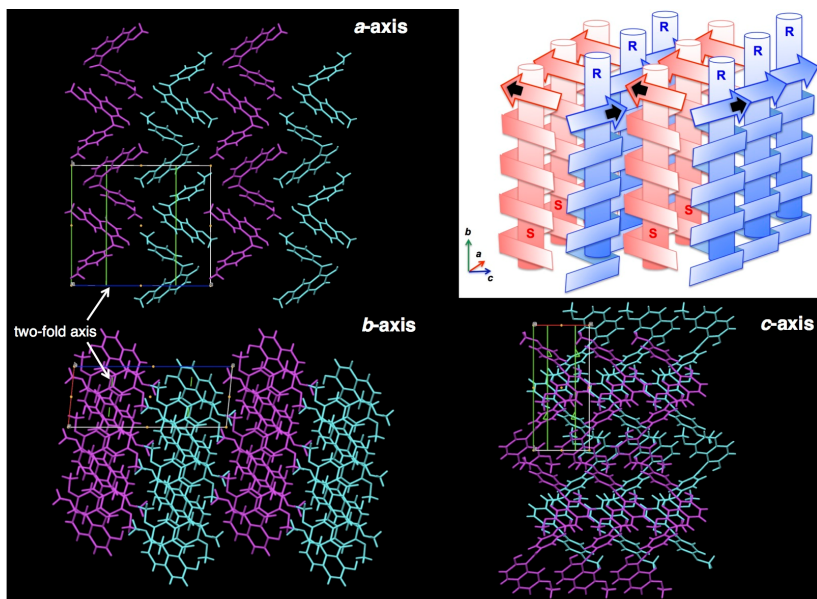


**Figure 8.** Single molecular structure of homologous compound with intramolecular O-H...O=C hydrogen bond (see ref. [14]).

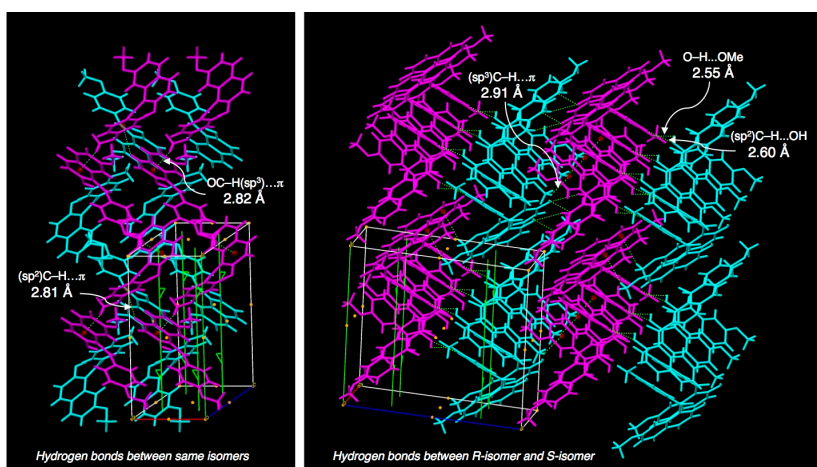
*S*-Enantiomeric molecules of the left-handed  $2_1$  helical assemblies are connected to the *R*-enantiomeric molecules of the right-handed ones by two types of non-covalent bonding interactions along *ac*-diagonal, *i.e.*, head-to-tail-typed O-H...OMe {benzoyl} classical hydrogen bond [2.55 Å] and {benzoyl}  $(sp^2)C-H...OH$  non-classical hydrogen bond [2.60 Å], and tail-to-tail(head-to-head)-typed {naph}OC-H( $sp^3$ )... $\pi$  {naph} non-classical hydrogen bonds [2.91 Å] (Figure 10, right).

Non-covalent bonding interactions of title molecule and the homologous molecule are classified by types and distances as shown in Table 3. Non-covalent bonding distances between same enantiomeric molecules are exhibited with red characters, and those between opposite-enantiomeric molecules are shown as blue characters. Besides, non-covalent bonding distances between *R(S)*-enantiomeric molecule of conformer A and *R(S)*-enantiomeric molecule of conformer B are expressed

as orange characters, and those between *R(S)*-enantiomeric molecule of conformer A and *S(R)*-enantiomeric molecule of conformer B are shown as purple characters. As common features of title compound and the homologous compound, O-H...O=C classical hydrogen bonds are observed in their crystals. However, the O-H...O=C classical hydrogen bond in homologous compound is intramolecularly formed. Individual features of title compound and homologous compound are described below. In homologous molecule, O-H...OMe classical hydrogen bonds and {benzoyl} $(sp^2)C-H...OH$  non-classical hydrogen bonds are formed between opposite-enantiomeric molecules, *i.e.*, between *R*-enantiomeric molecule and *S*-enantiomeric one. They are observed along *ac*-diagonal, and the distances are approximately same (2.55 and 2.60 Å). The C-H... $\pi$  non-classical hydrogen bonds are formed between same enantiomeric molecules, *i.e.*, between *R(S)*-enantiomeric molecules.



**Figure 9.** Molecular packing structures of homologous compound viewed down three directions: *R*-enantiomeric isomer and *S*-enantiomeric isomer are expressed as pale blue-colored molecule and pink-colored molecule, respectively.



**Figure 10.** Hydrogen bonds in crystal of homologous compound: hydrogen bonds between same enantiomeric molecules (left) and hydrogen bonds between opposite-enantiomeric molecules (right).

**Table 3.** Non-covalent bonding interactions in title compound and the homologous compound (Å)

| Interactions                               | Homologue | Title compound |             |
|--|-----------|----------------|-------------|
|  |           | Conformer A    | Conformer B |
| O-H...O=C (Intra)                          | 1.79      | -              | -           |
| O-H...O=C                                  | -         | 1.94           | 1.92        |
| O-H...OMe{benzoyl}                         | 2.55      | -              | -           |
| {benzoyl}(sp <sup>2</sup> )C-H...O=C       | -         | 2.44           | 2.50        |
| {benzoyl}(sp <sup>2</sup> )C-H...OMe       | -         | -              | 2.57        |
| {naph}OC-H(sp <sup>3</sup> )...O=C         | -         | -              | 2.58        |
| {benzoyl}(sp <sup>2</sup> )C-H...OH        | 2.60      | -              | -           |
| {naph}(sp <sup>2</sup> )C-H...OH           | -         | 2.62           | -           |
| {naph}OC-H(sp <sup>3</sup> )...π {benzoyl} | -         | 2.71           | -           |
| {naph}OC-H(sp <sup>3</sup> )...π {naph}    | -         | -              | 2.80        |
| {naph}(sp <sup>2</sup> )C-H...π {naph}     | 2.81      | -              | -           |
| {benzoyl}OC-H(sp <sup>3</sup> )...π {naph} | 2.82      | -              | -           |
| {naph}(sp <sup>2</sup> )C-H...π {benzoyl}  | -         | -              | 2.83        |
| {naph}(sp <sup>2</sup> )C-H...π {naph}     | -         | -              | 2.90        |
| {naph}OC-H(sp <sup>3</sup> )...π {naph}    | 2.91      | -              | -           |

Red characters = Non-covalent bonding distances between same enantiomeric molecules; blue characters = non-covalent bonding distances between opposite-enantiomeric molecules; orange characters = non-covalent bonding distances between *R(S)*-enantiomeric molecule of conformer A and *R(S)*-enantiomeric molecule of conformer B; purple characters: non-covalent bonding distances between *R(S)*-enantiomeric molecule of conformer A and *S(R)*-enantiomeric molecule of conformer B. Under lines indicate that the moiety is in conformer A.

They are observed along *a*-axis, and the distances are almost same (2.81 and 2.82 Å). On the other hand, title molecule shows converse relation with the homologous molecule in kinds of hydrogen bonds and the counter molecule's absolute configuration. O-H...O=C Classical hydrogen bonds and C-H...O non-classical hydrogen bonds are observed between same enantiomeric molecules (red characters).

The C-H... $\pi$  non-classical hydrogen bonds are formed between opposite-enantiomeric molecules (blue characters). In conformer A, there is large difference in the non-covalent bonding distances between same enantiomeric molecules as classical O-H...O=C hydrogen bonds (1.94 Å), non-classical {benzoyl}(sp<sup>2</sup>)C-H...O=C hydrogen bonds (2.44 Å), and non-classical {naph}(sp<sup>2</sup>)C-H...OH hydrogen bonds (2.62 Å). The gap seems to be bridged by non-classical hydrogen bonds among conformer A and conformer B (orange characters), {benzoyl(B)}(sp<sup>2</sup>)C-H...OMe(A) hydrogen bonds (2.57 Å) and {naph(B)}OC-H(sp<sup>3</sup>)...O=C(A) hydrogen bonds (2.58 Å). Conformer B essentially plays same role for hydrogen bonds between opposite-enantiomeric molecules of conformer A (purple characters). *S*-Enantiomeric molecules of conformer A are connected with *R*-enantiomeric ones of conformer A by only C-H... $\pi$  {naph}OC-H(sp<sup>3</sup>)... $\pi$ {benzoyl} hydrogen bonds (2.71 Å) (blue characters). *R*-Enantiomeric molecules of conformer B seem to form contact alignment of *S*-enantiomeric ones of conformer A by formation of three types of weak C-H... $\pi$  hydrogen bonds with *S*-enantiomeric molecules of conformer A (purple characters), {naph(A)}OC-H(sp<sup>3</sup>)... $\pi$ {naph(B)} hydrogen bond (2.80 Å), {naph(B)}(sp<sup>2</sup>)C-H... $\pi$ {benzoyl(A)} hydrogen bond (2.83 Å), and {naph(A)}(sp<sup>2</sup>)C-H... $\pi$ {naph(B)} hydrogen bond (2.90 Å).

Direction of classical hydrogen bonding interactions seems to be related with the spatial distance of hydroxy group from chiral axis.

Classical hydrogen bonds are formed between opposite-enantiomeric molecules when hydroxy group is situated at vicinal position of the chiral axis such as homologous molecule, whereas those are formed between same enantiomeric molecules when the hydroxy group is positioned far from the chiral axis as title compound. The direction of classical hydrogen bonds influences to balanced formation of non-classical hydrogen bonds. When classical hydrogen bonds are formed between opposite-enantiomeric molecules as shown in homologous compound, non-classical hydrogen bonds between same enantiomeric molecules and those between opposite-enantiomeric molecules are almost same distances, respectively (2.81 and 2.82 Å for non-classical hydrogen bonds between same enantiomeric molecules; 2.55 and 2.60 Å for non-classical hydrogen bonds between opposite-enantiomeric molecules). However, non-classical hydrogen bonds are obliged to take an imbalance state when classical hydrogen bonds are formed between same enantiomeric molecules as shown in conformer A of title compound (2.44 and 2.62 Å). The independent molecules are considered to act an intermediate to each other to adjust the imbalance of non-classical hydrogen bonds and reinforce the spatial packing of molecules together.

#### 4. Conclusion

Conclusively, comparison of spatial organization of title compound and the homologous compound reveals the characteristic relation between the position of hydroxy group in molecules and accumulation structure of these pairs of isomeric aromatic rings combination compounds. Both isomeric compounds have sole hydroxy group capable for forming classical hydrogen bonding. The position of the hydroxy group in single molecular structure determined the place of the hydrogen bondings. The intermolecular classical

hydrogen bonding is observed in both of title compounds and homologous one. On the other hand, intramolecular classical one is confirmed only in homologous compound. The position and the direction of the strongest non-covalent bonding interaction are presumed to govern the diversity of the crystal system of these compounds. The intermolecular classical hydrogen bonding makes contact alignment of molecules in one direction, which bring about small flexibility of conformation of molecules resulting in requirement of assistance of another conformer (independent molecule) to achieve the dense packing of molecules. Two kinds of conformers with enantiomers realize the stable crystal packing cooperatively. On the other hand, the homologous compound, which consumes the strongest classical hydrogen bonding in the core part of molecules, are considered to make most fitted conformation for rather depressed intermolecular classical hydrogen bonding and other non-classical hydrogen bondings realizing favourable conformation in enthalpy and symmetry, without presence of independent molecules.

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#### Supplementary material

All crystallographic data for this paper are deposited in Cambridge Crystallographic Data Centre (CCDC 1520592). The data can be obtained free of charge at [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk) or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 (0) 1223 336033, e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)

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