



CRYSTAL STRUCTURE OF 2,7-DIMETHOXY-1,8-BIS(1-NAPHTHOYL)NAPHTHALENE: COOPERATIVE HYDROGEN BONDS AND THEIRS ROLE IN THE MOLECULAR PACKING

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Keywords: Non-coplanarly accumulated aromatic rings molecule, Cooperative hydrogen bonds, Orientation of 2₁ helical assembly

The aromatic rings in 2,7-dimethoxy-1,8-bis(1-naphthoyl)naphthalene in crystal accumulate non-coplanarly to each other, with the dihedral angle between the terminal naphthalene and the 2,7-dimethoxynaphthalene rings of closer to 90° than the homologous compounds, 1,8-dibenzoyl-2,7-dimethoxynaphthalene and 2,7-dimethoxy-1,8-bis(2-naphthoyl)naphthalene. Molecular packing structures of the title compound and the homologous two compounds are classified by screw-sense and orientation of molecular assembly with a two-fold screw axis. In the title compound, right(left)-handed 2¹ helical assemblies are oriented in a *downward* (an upward) direction forming a plane. The plane is alternately stacked with the counter handed version. In the homologous compounds, right (left)-handed 2¹ helical assemblies are oriented in an *upward* (a downward) direction to form a plane. In other words, the 2¹ helical assemblies in the molecular packing of the title compound correspond to the 180° rotated one of the homologous compounds as space geometry. In the right(left)-handed 2¹ helical assembly of the title compound, *two types* of effective C–H...O=C hydrogen bonds are observed, i.e., (sp³)C–H...O=C hydrogen bond and (sp²)C–H...O=C hydrogen bond. On the other hand, either of two types of C–H...O=C hydrogen bonds is found in a right(left)-handed 2¹ helical assembly of the homologous two compounds. Besides, the title compound has (sp³)C–H...O=C hydrogen bonds between the right-handed 2¹ helical assembly and the left-handed one, and the homologous two compounds have effective π...π stacking interactions and (sp²)C–H...O=C hydrogen bonds. Cooperative two types of C–H...O=C hydrogen bonds in right(left)-handed helical assembly induce a *downward* (an upward) orientation of the 2¹ helical assemblies, showing P2₁/c space group. Sole function of either (sp³)C–H...O=C hydrogen bond or (sp²)C–H...O=C one in right(left)-handed helical assembly leads the opposite oriented right(left)-handed 2¹ helical assemblies, showing C2/c space group.

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in front of a two-fold screw axis inclined to the right or left, the assemblies can be defined to be right- or left-handed, respectively.^{8,9} They have focused on a series of compounds forming molecular assembly with 2¹ screw axis in the CSD (the Cambridge Structure Database), and analyzed the correlation of the handedness of 2¹ helical assembly and molecular interactions.¹⁰

Introduction

Molecular interactions have gained growing interest for one of the property realizing factors as well as concrete covalent chemical bonding in wide-range of chemistry including pharmaceutical chemistry, organic chemistry and material chemistry, e.g., molecular recognition of supramolecular materials, expression of regio- and chemoselectivity in organic reaction.¹ Organic crystals are composed of organic molecules arranged spatially by the molecular interactions such as hydrogen bonds and van der Waals interactions,² which are far weaker than covalent bonds. In other words, organic crystals can be regarded as *flexible* solid structure. From this point of view, to employ organic crystal as model or probe for molecular interaction analysis is rational. Organic crystals sometimes show interesting phenomena of polymorphs³ and phase transition by heat and pressure,⁴ and characteristic properties on the basis of the molecular accumulation structures such as light emission and electric properties.^{5,6} Understanding the role of non-bonding interactions in/among molecules is one of important aspects of organic crystal chemistry for design of organic crystal showing desirable properties.⁷ Miyata and the colleagues have demonstrated an elegant concepts to reveal expression of chirality in organic crystals, a so-called supramolecular-tilt-chirality method, i.e., for the molecules

Several years ago, the authors have found that electrophilic aromatic substitution reaction of 2,7-dialkoxynaphthalene with benzoyl chloride derivative affords *peri*(1,8)-diarylated naphthalene compounds with high regioselectivity and conversion.¹¹ By changing the substituent on the benzoyl chloride, various *peri*-arylnaphthalene compounds were obtained in reasonable yields, e.g., symmetrically and unsymmetrically substituted *peri*-arylnaphthalene compounds. Fortunately, *peri*-arylnaphthalene compounds tend to afford single crystals suitable for X-ray crystallography. The single molecular structure and the structural features of the molecular packing for roughly eighty *peri*-arylnaphthalene compounds and the homologues have been reported by the authors' group.¹² There are two common features in single molecular structure of *peri*-arylnaphthalene compounds: 1) two aryl groups are attached in a nearly perpendicular fashion against the naphthalene rings and 2) two aryl groups are oriented in opposite direction each other form almost all homologous and analogous arylnaphthalene compounds. In the crystal packing, non-bonding interactions arising from the chemically modified moieties are distinguishable from those by the original aromatic rings-accumulated framework. Under these circumstances, the authors have attempted to clarify effect of substituents of the benzoyl groups in *peri*-arylnaphthalene compounds on molecular packing

structure through the systematic comparison of non-bonding interactions.¹³⁻²¹ Herein, the crystal structure of novel *peri*-aroylnaphthalene compound, 2,7-dimethoxy-1,8-bis(1-naphthoyl)naphthalene (**1**)²² is reported and the difference in both single crystal structure and crystal packing structure is discussed by comparing with those of the substituent-free type homologues, 1,8-dibenzoyl-2,7-dimethoxynaphthalene (**2**)²³ and the regioisomer of 2,7-dimethoxy-1,8-(2-naphthoyl)naphthalene (**3**)²⁴ to clarify the influence of the modification of the aromatic rings-accumulated framework and the role of molecular interactions in the molecular packing (**Figure 1**).

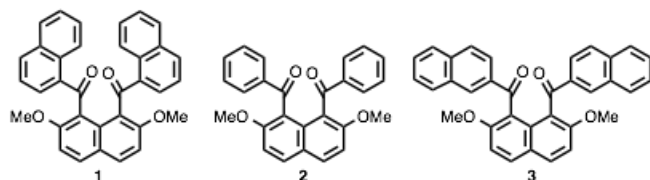
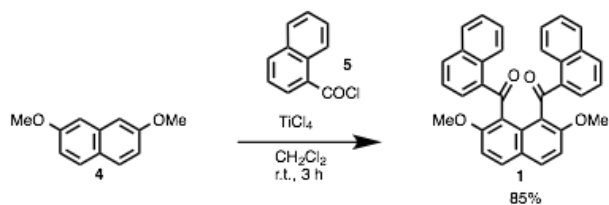


Figure 1 2,7-dimethoxy-1,8-bis(1-naphthoyl)naphthalene (**1**) and the homologues **2** and **3**.

Results and discussion

The title compound (**1**) was synthesized *via* electrophilic aromatic substitution mediated by TiCl_4 of 2,7-dimethoxynaphthalene (**4**) with 1-naphthoyl chloride (**5**) (**Scheme 1**). This reaction proceeded with high efficiency (85% yield). Single crystals suitable for X-ray analysis were obtained by recrystallization from chloroform and methanol.



Scheme 1. Synthesis of 2,7-dimethoxy-1,8-bis(1-naphthoyl)naphthalene (**1**).

Figure 2 gives *ORTEP* representation of the molecular structure of the title compound (**1**), as determined by the structured X-ray analysis.²² **Table 1** shows the crystallographic data of the title compound (**1**). **Table 2** shows selected bond lengths and angles. **Table 3** gives selected torsion angles. The nonbonding distances are listed in **Table 4**.

In molecular structure of title compound **1**, the two naphthoyl groups are twisted away from the 2,7-dimethoxynaphthalene moiety, and oriented in an opposite direction. Dihedral angles between the naphthalene rings of 1-naphthoyl groups and the 2,7-dimethoxynaphthalene moiety are 89.84° and 85.06° [torsion angles = $-77.8(4)^\circ$ ($\text{O1}-\text{C11}-\text{C1}-\text{C9}$) and -70.64° ($\text{O2}-\text{C22}-\text{C8}-\text{C9}$)]. Furthermore, the terminal naphthalene rings of the 1-naphthoyl moieties make large dihedral angle of 49.12° .

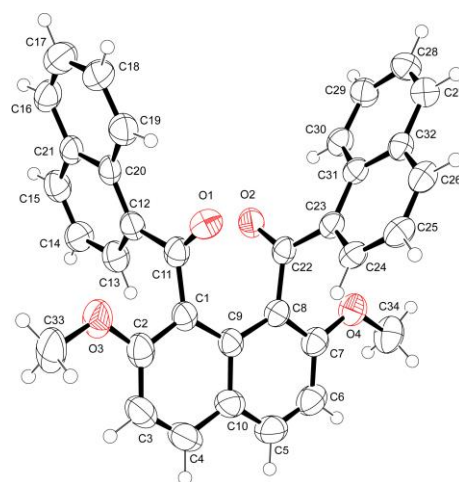


Figure 2 Molecular structure of 2,7-dimethoxy-1,8-bis(1-naphthoyl)naphthalene (**1**), with the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level.

Table 1. Crystallographic data and structure refinement parameters of title compound

Empirical formula	$\text{C}_{34}\text{H}_{24}\text{O}_4$
Formula weight	496.53 g mol^{-1}
Crystal shape, colour	Needle, colourless
Temperature	173 K
Wavelength	1.54187 Å
Crystal system	Monoclinic
Space group	$P21/c$
Unit cell dimensions	$a = 19.551(6)$ Å $b = 8.229(2)$ Å $c = 16.529(5)$ Å $\alpha = 90.00^\circ$ $\beta = 111.547(4)^\circ$ $\gamma = 90.00^\circ$
Volume	2473.5 (12) Å ³
Z	4
Calculated density	1.333 Mg m^{-3}
Absorption coefficient	0.09 mm^{-1}
$F(000)$	1040
Crystal size	0.40 × 0.30 × 0.20 mm
θ range for data collection	2.2 to 26.5°
Limiting indices	$-19 \leq h \leq 24$ $-10 \leq k \leq 10$ $-20 \leq l \leq 20$
Reflections collected/unique	18194/5120 [$R_{\text{int}}=0.030$]
Completeness to $\theta=26.5^\circ$	99.7%
Max. and min. transmission	0.9829 and 0.9662
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5120/0/345
Goodness-of-fit on F^2	1.123
Final R indices	$R(F^2) = 0.085$, $wR(F^2) = 0.2164$
$[F^2 > 2\sigma(F^2)]$	$R(F^2) = 0.1016$, $wR(F^2) = 0.2293$
R indices (all data)	
Largest diff. peak and hole	0.63 $\text{e} \text{Å}^{-3}$ and $-0.22 \text{ e} \text{Å}^{-3}$

Table 2. Selected bond lengths (Å) and angles (°) of molecule **1**.

Bond lengths		Bond angles	
O1–C11	1.2164 (4)	O1–C11–C12	124.1 (3)
C11–C12	1.507 (4)	O1–C11–C1	119.2 (3)
C1–C9	1.5158 (19)	C1–C9–C8	125.1 (3)
C1–C2	1.389 (4)	C2–C1–C11	115.0 (3)
C11–C12	1.507 (4)	C13–C12–C11	118.1 (3)
C12–C13	1.363 (4)	C20–C12–C11	123.7 (3)
C12–C20	1.409 (4)	O2–C22–C23	123.3 (3)
O2–C22	1.223 (3)	O2–C22–C8	118.5 (3)
C22–C24	1.490 (4)	C7–C8–C22	116.1 (3)
C8–C9	1.432 (4)	C24–C23–C22	118.2 (3)
C7–C8	1.380 (4)	C31–C23–C22	122.4 (3)
C22–C23	1.490 (4)		
C23–C24	1.391 (4)		
C23–C31	1.429 (4)		

Table 3. Selected torsion angles (°) of molecule **1**.

Linkage	Angle
O1–C11–C1–C2	102.8 (3)
O1–C11–C1–C9	–77.8 (4)
O1–C11–C12–C13	163.6 (3)
O1–C11–C12–C20	–14.7 (5)
C1–C11–C12–C13	–17.9 (4)
C1–C11–C12–C20	163.9 (3)
O2–C22–C8–C7	105.6 (3)
O2–C22–C8–C9	–70.6 (4)
O2–C22–C23–C24	152.6 (3)
O2–C22–C23–C31	–24.3 (4)
C8–C22–C23–C24	–27.0 (4)
C8–C22–C23–C31	156.0 (3)
C8–C9–C1–C11	4.1 (5)
C1–C9–C8–C22	–0.1 (4)

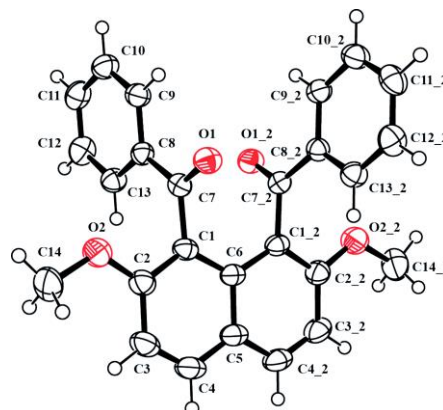
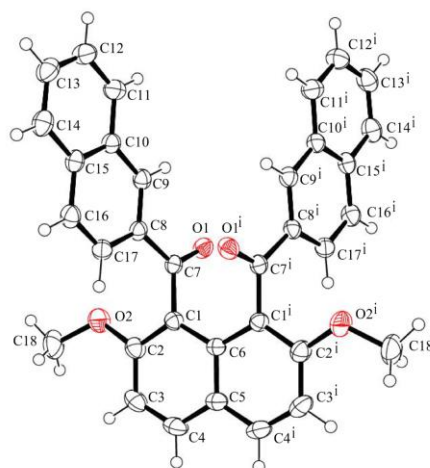
Table 4. Nonbonding distances and related geometrical parameters in 2,7-dimethoxy-1,8-bis(1-naphthoyl)naphthalene (**1**).

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (deg.)
C33–H33A...O2 ⁱ	0.98	2.49	3.390 (5)	152
C34–H34B...O1 ⁱⁱ	0.98	2.44	3.377 (4)	161
C29–H29...O1 ⁱ	0.95	2.582	3.512 (4)	166
C3–H3...O2 ⁱ	0.95	2.678	3.196	140

Symmetry codes: (i) $x, y-1, z$; (ii) $x, -y+1/2, z-1/2$.

Figure 3 and **Figure 4** exhibit X-ray crystal structures of the homologous *peri*-aroylnaphthalene compounds, 1,8-dibenzoyl-2,7-dimethoxynaphthalene (**2**) and 1,8-bis(2-naphthoyl)-2,7-dimethoxynaphthalene (**3**) (For crystallographic data, see Table S-1).^{23,24} The molecule of 1,8-dibenzoyl-2,7-dimethoxynaphthalene (**2**) possesses crystallographically imposed twofold C_2 symmetry. Therefore, the asymmetric unit contains one-half of the molecule. Thus, the two benzoyl groups are oriented in an opposite direction. The two benzene rings of the benzoyl groups are situated to the naphthalene ring with dihedral angle of 80.25(6)°, and placed in an almost parallel fashion to each other with dihedral angle of 12.18°. Compound **3**, 1,8-(2-naphthoyl)-2,7-dimethoxynaphthalene, has deep similarities to the benzoyl group-bearing homologue **2** in single molecular structure. The molecule of 1,8-(2-naphthoyl)-2,7-

dimethoxynaphthalene (**3**) lies across a crystallographic two-fold axis. Dihedral angle between the terminal naphthalene ring and 2,7-dimethoxynaphthalene and that between terminal naphthalene rings are 75.13(4)° and 5.21(5)°, respectively.

**Figure 3.** Molecular structure of 1,8-dibenzoyl-2,7-dimethoxynaphthalene (**2**), with the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level. The symbol “_2” refers to symmetry code: $-x, y, -z + 1/2$.**Figure 4** Molecular structure of 2,7-dimethoxy-1,8-bis(2-naphthoyl)naphthalene (**3**), with the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level. The symbol “ⁱ” refers to symmetry code: $-x+1, y, -z+1/2$.

In title compound **1**, dihedral angle between the terminal naphthalene ring and 2,7-dimethoxynaphthalene moiety is closer to 90° than other two homologues. Furthermore, the dihedral angle between the terminal naphthalene rings is larger than the two homologues, i.e., 49.12° > 12.18° (molecule **2**) > 5.21° (molecule **3**). These results indicate that title compound **1** has large internal steric repulsion.

Figure 5, **Figure 6**, and **Figure 7** show the crystal structure of title compound **1** and the homologues **2** and **3** with symmetry elements. In molecular packing of title compound **1**, the molecules related to two-fold screw axis form two types of helical structures, i.e., right-handed 2^1 helical assembly and left-handed one. Right-handed 2^1 helical assemblies are oriented in a *same* direction, and aligned along *a* axis forming a plane (**Figure 5**, bottom). Left-handed 2^1 helical assemblies are oriented in an opposite direction to the right-handed ones, and aligned along *a* axis.

The plane composed of right-handed 2^1 helical assemblies and that composed of left-handed 2^1 helical assemblies are alternately stacked into stripe structure along c axis.

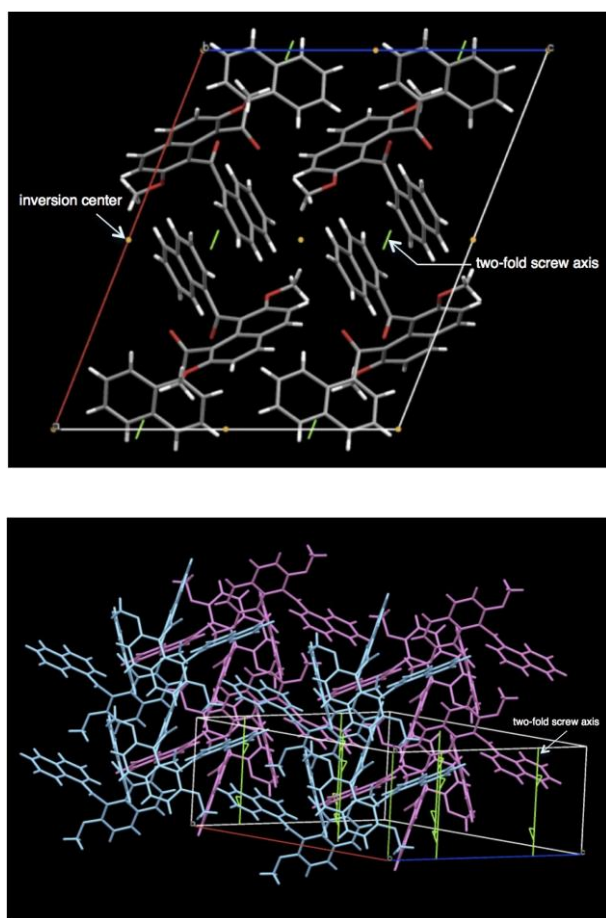


Figure 5. Molecular packing structure of 2,7-dimethoxy-1,8-bis(1-naphthoyl)naphthalene (**1**) with symmetry elements: Molecular packing viewed down b axis (top). Colour-coded molecular packing according to screw-sense of 2^1 helical assembly (bottom). Right-handed 2^1 helical assembly and left-handed one are expressed as blue molecules and pink molecules, respectively.

In the cases of the homologues **2** and **3**, half of the molecules make 2^1 helical assembly. In a similar manner as title compound **1**, there are two types of 2^1 helical assemblies generated by two-fold screw axes.

Right(left)-handed 2^1 helical assemblies are aligned along a axis, however they are oriented in an *upward* (a downward) direction (**Figure 6** and **Figure 7**, bottom). The right(left)-handed 2^1 helical assemblies are alternately overlapped with the counter-handed version 2^1 helical assemblies along c axis. These features of molecular packing structure in each compound are illustrated as **Figure 8**. The 2^1 helical assemblies in the molecular packing of the title compound **1** correspond to the 180° rotated one of the homologous compounds **2** and **3** as space geometry.

Molecular interactions elucidated on the basis of shorter distance of two atoms less than the sum of the van der Waals radii are observed in right(left)-handed 2^1 helical assembly and between right-handed 2^1 helical assembly and left-handed one (**Figures 9–11**).

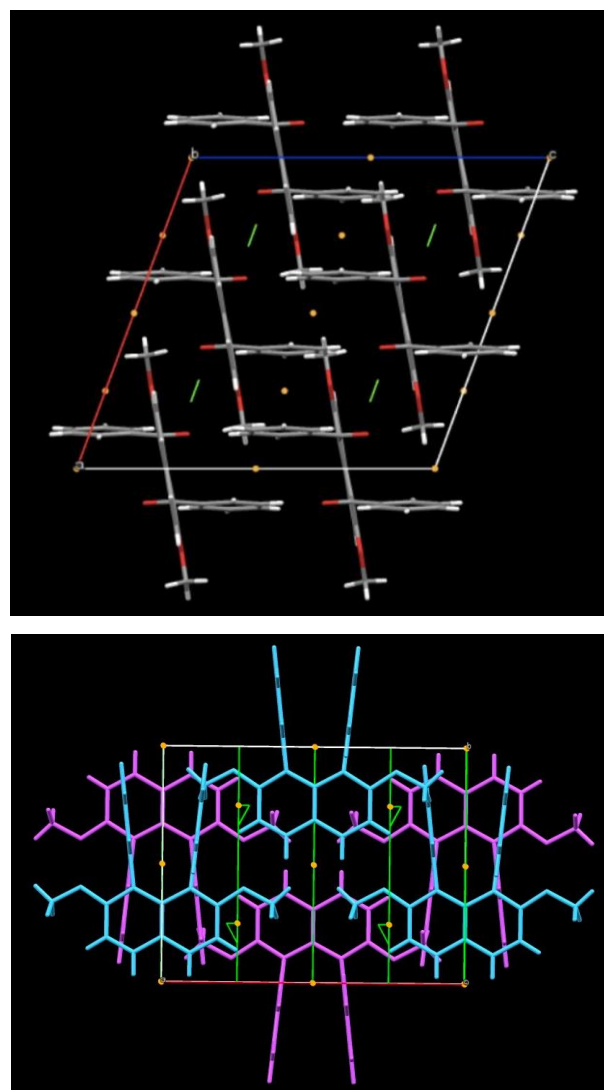
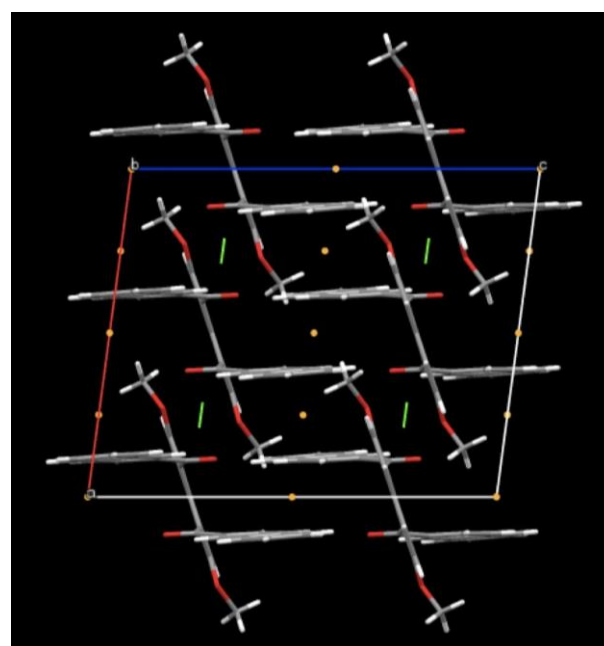


Figure 6. Molecular packing structure of 1,8-dibenzoyl-2,7-dimethoxynaphthalene (**2**) with symmetry elements: Molecular packing viewed down b axis (top). Colour-coded molecular packing according to screw-sense of 2^1 helical assembly (bottom).



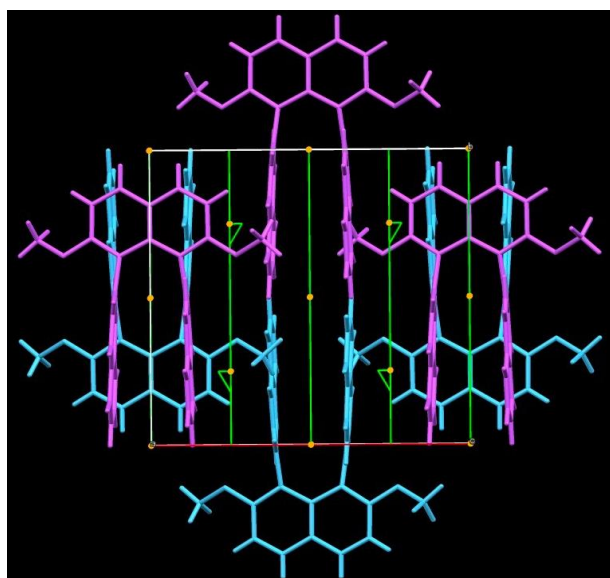


Figure 7. Molecular packing structure of 2,7-dimethoxy-1,8-bis(2-naphthoyl)naphthalene (**3**) with symmetry elements: Molecular packing viewed down b axis (top). Colour-coded molecular packing according to screw-sense of 2^1 helical assembly (bottom).

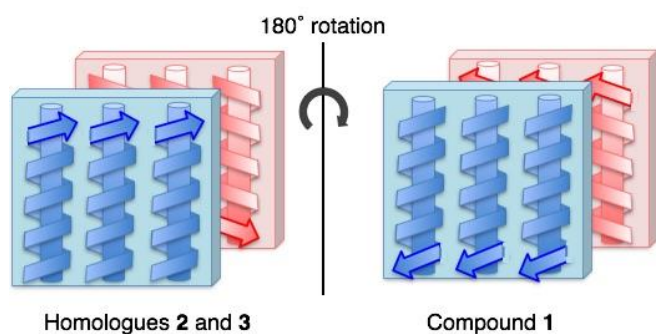


Figure 8 Molecular packing structures of compounds **1**, and homologues **2** and **3** illustrated with 2^1 helical assemblies.

In title compound **1**, two types of C–H...O=C hydrogen bonds, (sp^3)C–H...O=C hydrogen bonds [C33–H33A...O2ⁱ = 2.492 Å, symmetry code: (i) $x, -y+1, z$] and relatively weak two (sp^2)C–H...O=C ones [C29–H29...O1ⁱ = 2.582 Å, C3–H3...O2ⁱ = 2.678 Å, symmetry code: (i) $x, -1+y, z$] are observed in a right(left)-handed 2^1 helical assembly (**Figure 9**, top). In addition, (sp^3)C–H...O=C hydrogen bonds [C34–H34B...O1ⁱⁱ = 2.44 Å, symmetry code: (ii) $x, -y+1/2, z-1/2$] are observed between the right-handed 2^1 helical assembly and the left-handed one (**Figure 9**, bottom). In molecular packing of 1,8-dibenzoyl-2,7-dimethoxynaphthalene (**2**), (sp^3)C–H...O=C hydrogen bonds (2.391 Å) are observed in a right(left)-handed 2^1 helical assembly (**Figure 10**, top). On the other hand, the right-handed 2^1 helical assembly and the left-handed one are connected through (sp^2)C–H...O=C hydrogen bonds (2.597 Å) in opposite direction (**Figure 10**, bottom). In addition, π ... π stacking interactions between benzene rings [centroid–centroid and interplanar distances of 3.6383(10) Å and 3.294 Å, respectively] are observed in parallel to the (sp^2)C–H...O=C hydrogen bonds (2.597 Å). Molecules of 2,7-dimethoxy-1,8-bis(2-naphthoyl)naphthalene (**3**) form

essentially similar intermolecular interactions to the benzoyl group-bearing homologue (**2**). Hydrogen bonds of (sp^2)C–H...O=C (2.590 Å) are observed in a right(left)-handed 2^1 helical assembly (**Figure 11**, top). Hydrogen bonds of (sp^2)C–H...O=C (2.491 Å) and π ... π stacking interactions between naphthalene rings in 2-naphthoyl groups [centroid–centroid and interplanar distances of 3.6486(8) Å and 3.3734(5) Å, respectively] link the right(left)-handed 2^1 helical assembly and the left(right)-handed one in opposite direction (**Figure 11**, bottom). The above intermolecular interactions are summarized in **Table 5**. In molecular packing of title compound **1**, strong (sp^3)C–H...O=C hydrogen bond and weak (sp^2)C–H...O=C hydrogen bonds cooperatively stabilize the right(left)-handed 2^1 helical assembly. Hydrogen bond (sp^3)C–H...O=C also contributes to connect the right-handed 2^1 helical assembly and the left-handed one. On the other hand, molecular packing of homologues **2** and **3** has either of (sp^3)C–H...O=C hydrogen bond or (sp^2)C–H...O=C hydrogen bond as the predominant interaction in the right(left)-handed 2^1 helical assembly. Additionally, π ... π stacking interaction and (sp^2)C–H...O=C hydrogen bond connect with the right-handed 2^1 helical assembly and the left-handed one.

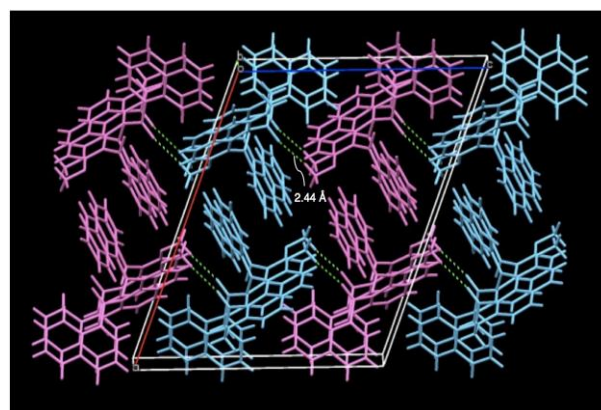
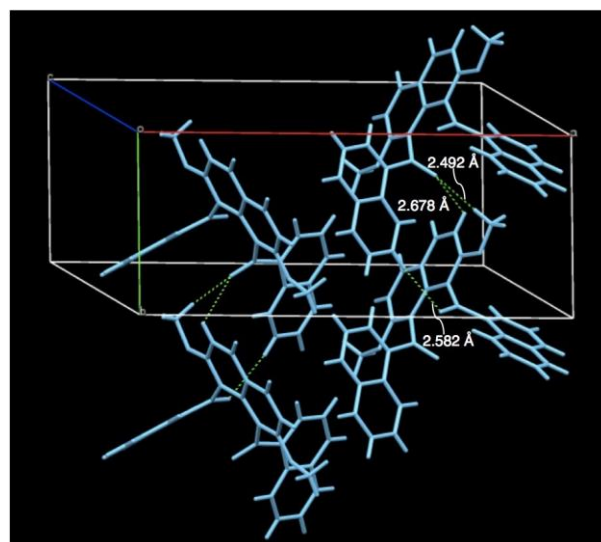


Figure 9. Intermolecular hydrogen bonds in molecular packing structures of 2,7-dimethoxy-1,8-bis(1-naphthoyl)naphthalene (**1**): Molecules are colour-coded according to sense of 2^1 helical assembly. Intermolecular hydrogen bonds in a right-handed 2^1 helical assembly (top) and intermolecular hydrogen bonds between right-handed 2^1 helical assembly and left-handed one (bottom).

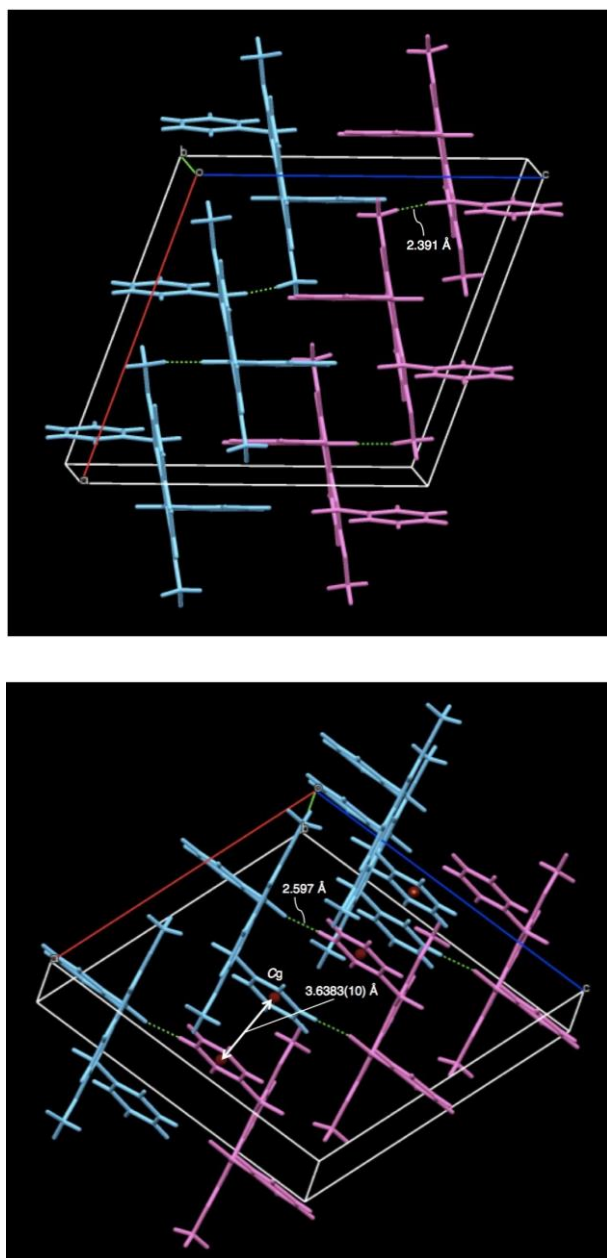


Figure 10. Intermolecular hydrogen bonds in molecular packing structures of 1,8-dibenzoyl-2,7-dimethoxynaphthalene (**2**): Intermolecular hydrogen bonds in a right(left)-handed 2^1 helical assembly (top) and intermolecular hydrogen bonds between right-handed 2^1 helical assembly and left-handed one (bottom). C_g is the centroid of the C8–C13 ring.

Either (sp^3)C–H...O=C hydrogen bond or (sp^2)C–H...O=C one in a right(left)-handed 2^1 helical assembly has no contribution to form the planar accumulation of the downward (upward) oriented right(left)-handed 2^1 helical assemblies for homologues **2** and **3**. When two types of C–H...O=C hydrogen bonds cooperatively stabilize a right(left)-handed 2^1 helical assembly, the right(left)-handed 2^1 helical assemblies are oriented in a downward (an upward) direction as 2,7-dimethoxy-1,8-bis(1-naphthoyl)naphthalene (**1**). Formation of (sp^3)C–H...O=C hydrogen bond between the right-handed 2^1 helical assembly and the left-handed one scarcely influence into the “cooperative” C–H...O=C hydrogen bonds in the right(left)-handed 2^1 helical assembly. However, π ... π stacking interactions between the right-handed 2^1 helical assembly and the left-handed one apparently mask the C–H...O=C

hydrogen bonds in the right(left)-handed 2^1 helical assembly. In other words, formation of cooperative C–H...O=C hydrogen bonds in the right(left)-handed 2^1 helical assembly determines space group of $P2_1/c$. Sole function of either two types of C–H...O hydrogen bonds in the right(left)-handed 2^1 helical assembly induce space group of $C2/c$ to the molecular packing. In the case of title compound **1**, the internal steric repulsion of the molecule seems to disturb overlapping of 1-naphthoyl rings with the adjacent molecules in the molecular packing. In consequence of this, two types of C–H...O=C hydrogen bonds stabilize the crystal structure of compound **1** in place of π ... π stacking interactions.

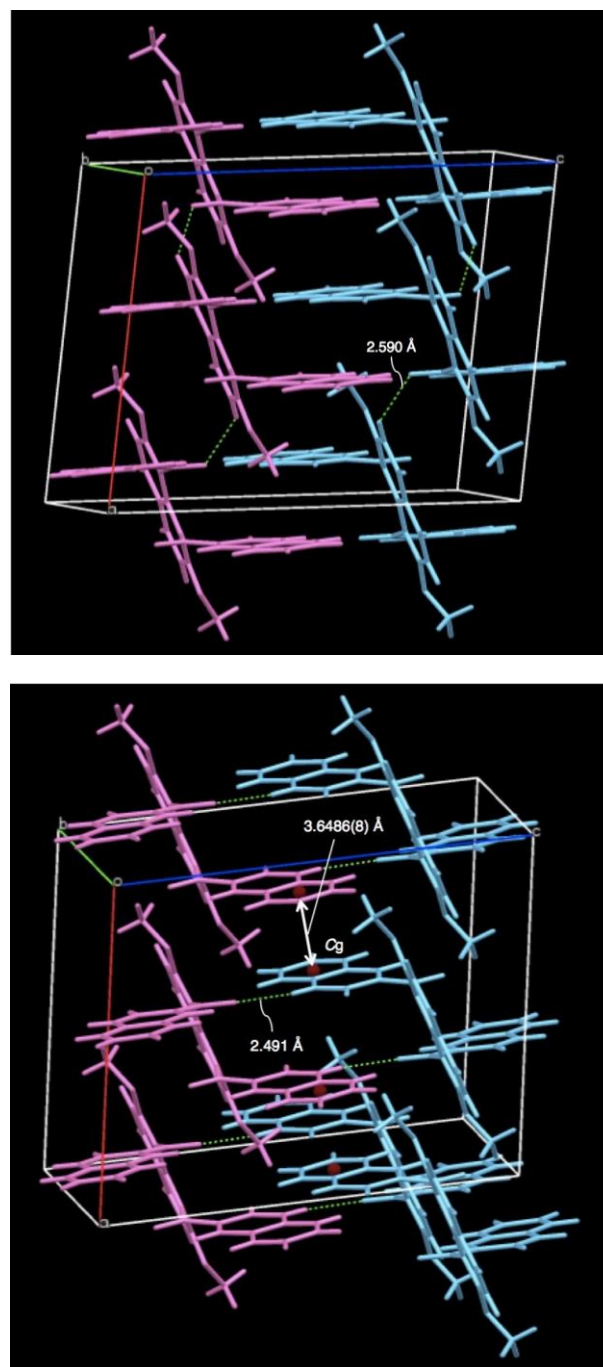


Figure 11 Intermolecular hydrogen bonds in molecular packing structures of 2,7-dimethoxy-1,8-bis(2-naphthoyl)naphthalene (**3**): Intermolecular hydrogen bonds in a right(left)-handed 2^1 helical assembly (top) and intermolecular hydrogen bonds between right-handed 2^1 helical assembly and left-handed one (bottom). C_g is the centroid of the C10–C15 ring.

Table 5. Nonbonding distances of 2,7-dimethoxy-1,8-bis(1-naphthoyl)naphthalene (**1**), and the homologues **2** and **3** (Å).

	Compound 1	Compound 2	Compound 3
<i>In right(left)-handed 2¹ helical assembly</i>			
(sp ³)C–H...O=C	2.492	2.391	-
(sp ²)C–H...O=C	2.582, 2.678	-	2.590
<i>Between right-handed 2¹ helical assembly and left-handed 2¹ one</i>			
(sp ³)C–H...O=C	2.44	-	-
(sp ²)C–H...O=C	-	2.597	2.491
π ... π stacking interaction			
Cg...Cg distance [interplanar distance]	-	3.6383(10) [3.294]	3.6486(8) [3.3734(5)]
Space group	P2 ₁ /c	C2/c	C2/c

Experimental

All reagents were of commercial quality and were used as received.²⁵ Solvents were dried and purified using standard techniques. 2,7-dimethoxynaphthalene (**4**) was prepared according to literatures.²⁶

Measurements

¹H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (300 MHz) and a JEOL ECX400 spectrometer (400 MHz). Chemical shifts are expressed in ppm relative to internal standard of Me₄Si (δ 0.00). ¹³C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (75 MHz). Chemical shifts are expressed in ppm relative to internal standard of CDCl₃ (δ 77.0). IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. High-resolution FAB mass spectra were recorded on a JEOL MStation (MS700) ion trap mass spectrometer in positive ion mode.

X-ray crystallography

For the crystal structure determination, the single-crystals of title compound and the homologues were used for data collection on a four-circle Rigaku RAXIS RAPID diffractometer (equipped with a two-dimensional area IP detector). The graphite-mono-chromated Cu K α 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 $F^2 > 2\sigma(F^2)$. The data collection and cell refinement were performed using *PROCESS-AUTO* software. The data reduction was performed using *CrystalStructure*. The structures were solved by direct methods using *SIR2004* and refined by a full-matrix least-squares procedure using the program *SHELXL97*. All H atoms were found in a difference map and were subsequently refined as riding atoms, with the aromatic C–H = 0.95 Å and methyl C–H = 0.98 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Synthesis of 2,7-dimethoxy-1,8-bis(1-naphthoyl)naphthalene(1)

To a solution of 2-naphthoyl chloride (**5**, 629.1 mg, 3.3 mmol) and TiCl₄ (1802.0 mg, 9.5 mmol) in CH₂Cl₂ (2.5 mL), 2,7-dimethoxynaphthalene (**4**, 188.2 mg, 1.0 mmol) was

added. The reaction mixture was stirred at rt for 3 h, then poured into ice-cold water (40 mL) and the aqueous layer was extracted with CHCl₃ (40 mL \times 3). The combined organic extracts were washed with 2 M aqueous NaOH (20 mL \times 3) followed by washing with brine (20 mL \times 3). The organic layer was dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to give a cake. The crude product was washed with chloroform (85 % yield). Furthermore, the isolated product was crystallized from methanol/chloroform (1:1, v/v) solution to give single crystals suitable for X-ray analysis.

2,7-dimethoxy-1,8-bis(1-naphthoyl)naphthalene (1)

Colourless needle (methanol/chloroform); m.p. = 604.0–606.0 K; IR (KBr) : 1665(C=O), 1607(Ar), 1511(Ar), 1264(OMe) cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 40°C): 3.54 (6H, s), 7.17–7.28 (6H, m), 7.22 (2H, d, J = 9.0 Hz), 7.58–8.00 (6H, m), 7.98 (2H, d, J = 9.0 Hz), 8.68 (2H, broad) ppm; HRMS (m/z) : [M+H]⁺ calcd. for C₃₄H₂₅O₄, 497.1753, found, 497.1751.

Synthesis of 1,8-dibenzoyl-2,7-dimethoxynaphthalene (2)

To a mixture of 2,7-dimethoxynaphthalene (0.200 mmol, 37.6 mg) and benzoic acid (0.440 mmol, 174 mg), P₂O₅–MsOH (0.88 mL) was added by portions at rt. After the reaction mixture was stirred at 60 °C for 3 h, it was poured into iced water (20 mL) and the mixture was extracted with CHCl₃ (15 mL \times 3). The combined extracts were washed with 2 M aqueous NaOH and followed by sat. NaCl aq. The organic layers thus obtained were dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure to give powdery product. Isolation of the title compound was carried out by column chromatography [hexane : AcOEt = 2 : 1 v/v] (1,8-diaroylnaphthalene 63%; 3-aroyleated naphthalene 19%; 1-aroyleated naphthalene 3%). Colourless single crystals suitable for X-ray diffraction were obtained by recrystallization from ethanol.

1,8-benzoyl-2,7-dimethoxynaphthalene (2)

Colourless needle (EtOH); m.p. = 530 K; IR (KBr): 1665, 1626 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 3.68 (6H, s), 7.21 (2H, d, J = 9.2 Hz), 7.34 (4H, dd, J = 7.6, 7.6 Hz), 7.49 (2H,

t, $J = 7.4$ Hz), 7.70 (4H, d, $J = 7.4$ Hz), 7.95 (2H, d, $J = 9.2$ Hz) ppm; ^{13}C NMR (75 MHz, CDCl_3): 56.40, 111.24, 121.47, 125.55, 127.95, 129.09, 129.84, 132.03, 132.64, 138.61, 156.28, 196.875 ppm. The above melting point and spectral data are compatible with the literature.²⁷

Synthesis of 2,7-dimethoxy-1,8-bis(2-naphthoyl)naphthalene (3)

To a solution of 2-naphthoyl chloride (629.1 mg, 3.3 mmol) and TiCl_4 (1802.0 mg, 9.5 mmol) in CH_2Cl_2 (2.5 mL), 2,7-dimethoxynaphthalene (188.2 mg, 1.0 mmol) was added. The reaction mixture was stirred at rt for 3 h, then poured into ice-cold water (40 mL) and the aqueous layer was extracted with CHCl_3 (30 mL \times 3). The combined organic extracts were washed with 2 M aqueous NaOH (20 mL \times 3) followed by washing with brine (20 mL \times 3). The organic layer was dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure to give a cake (72% yield). The crude product was purified by recrystallization from acetone (22% isolated yield). Furthermore, the isolated product was crystallized from acetone to give single crystals suitable for X-ray analysis.

2,7-dimethoxy-1,8-bis(2-naphthoyl)naphthalene (3)

Colourless block (acetone); m.p. = 505.0–506.0 K; IR (KBr): 1660(C=O), 1624(Ar), 1510(Ar), 1258(OMe) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 3.67 (6H, s), 7.26 (2H, d, $J = 9.0$ Hz), 7.37 (2H, t, $J = 7.5$ Hz), 7.45 (2H, t, $J = 7.5$ Hz), 7.68–7.77 (8H, m), 8.03 (2H, d, $J = 9.0$ Hz), 8.09 (2H, broad) ppm; ^{13}C NMR (75 MHz, CDCl_3) δ 56.47, 111.38, 121.73, 124.75, 125.64, 125.92, 127.54, 127.60, 127.83, 129.62, 130.16, 131.11, 132.17, 132.40, 135.50, 136.05, 156.52, 196.66 ppm; HRMS (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{25}\text{O}_4$, 497.1753; found, 497.1751.

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