CORRELATION OF MOLECULAR MOTIFS AND NON-CLASSICAL-HYDROGEN-BONDING INTERACTIONS IN CRYSTAL OF 2,7-DIMETHOXY-3-(1-NAPHTHOYL)NAPHTHALENE

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The crystal structure is reported for 2,7-dimethoxy-3-(1-naphthoyl)naphthalene (**1**), $C_{23}H_{17}O_3$, one of *β*-aroylated naphthalene compounds. In crystal, two naphthalene ring moieties of respective molecules are non-coplanarly located to each other, and two molecules are nested inside one another through a pair of C–H···π hydrogen-bonding interactions (C–H···*Cg* = 2.73 Å) forming a dimeric molecular aggregate. Each dimeric molecular aggregate is linked with four adjacent dimers by regular-squarely directed four (sp^3)C–H···OCH_3 hydrogen bonds between the methoxy groups (C–H···O = 2.50 Å) forming two-dimensionally spread plane. The planes are stacked into piles of layers along *ac* diagonal. On the other hand, the *β*-aroylated naphthalene homologues, 3-benzoylated naphthalene derivative **I** and 3-(2-naphthoylated) one **II**, are proved to take unidimensional molecular accumulation. Though each dimeric molecular aggregate has four identical interactions between adjacent dimeric molecular aggregates in crystal of homologue **I**, the rectangular, *i.e.*, non-regular-square aligned situation of four interactions makes the linkage of each aggregate with only two adjacent dimers resulting in ribbon structure. In crystal of homologue **II**, molecules are stacked without formation of dimeric aggregates in columnar structure. On the basis of the results of systematic comparison of molecular packing structure and effective noncovalent-bonding interactions among title compound **1** and the *β*-aroylated naphthalene homologues **I** and **II**, the presence of large difference in strength of intermolecular interactions, *i.e.*, predominant or apparently sole functioning of either C–H···O hydrogen bond or C–H···π hydrogen-bonding interaction induces only unidimensional molecular accumulation, *e.g.*, ribbon-like alignment composed of dimeric molecular aggregates or columnar assembling of molecules. ^{1}H NMR spectra suggest that conformational interconversion behaviour of title compound **1** through rotation around two kinds of C–C bonds in solution is disturbed rather largely compared to two homologous compounds **I** and **II**. Spatial organization characteristics of single molecular and molecular packing structures of *β*-aroylated naphthalene homologues in crystal are comparatively analyzed along with those in solution for the sake of elucidation of relationship among spatial organization, noncovalent bonding intermolecular interaction in crystal, and steric factors in solution.

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Introduction

Studies on molecular interactions in organic crystals[1] increase importance for many aspects of crystal engineering and materials design, for example, as a reply to the growing demands for fine-tuning of strength and effectiveness of the noncovalent-bonding interactions of crystal.[2,3] Recently, selective and exclusive electrophilic aromatic aroylation at α-/α,α'-(1-/1,8-) positions of naphthalene derivative has been found by the authors' group, which gives tandem aroylated products of 1-aroylated 2,7-dialkoxynaphthalene compounds as intermediating compounds and 1,8-diaroylated products as prolonged reacted ones.[4] Fortunately, the 1-aroylated and the 1,8–diaroylated naphthalene compounds are generally susceptible to affording qualified single crystals suitable for X-ray crystal analysis. The single molecular structure and the structural features of the molecular packing for roughly eighty compounds having 1,8-diaroylated naphthalene skeleton or the homologous/analogous structure have been reported by the authors' group *via* the Cambridge Structure Database (CSD).[5,6]

Molecular structures of 1,8-diaroylated 2,7-dialkoxynaphthalene compounds in crystals have common features that two aroyl groups are non-coplanarly situated to the 2,7-dialkoxynaphthalene core and oriented in an opposite direction along with a few exceptional compounds bearing unidirectional-aligned aroyl groups.[6] In the molecular packing of 1,8-diaroylated 2,7-dialkoxynaphthalene compounds, four kinds of noncovalent-bonding interactions, (sp^2)C–H···O=C hydrogen bond, (sp^3)C–H···O hydrogen bond, C–H···π hydrogen-bonding interaction, and π···π stacking are observed in decreasing order of frequency.[7] These observed crystal structural features indicate that the molecules of the 1,8-diaroylated naphthalene compounds are aggregated by significant contribution of non-classical hydrogen bonding interactions, which are generally recognized as weak molecular interactions in the crystal. To clarify such a curious situation, the authors have attempted to reveal correlation among single molecular structure, molecular packing structure, and effective non-classical hydrogen bonding

interactions by systematic comparison of crystal structures among designed 1,8-diaroylated naphthalene homologues.[8]

Recently, crystal structures of *β*-aroylated naphthalene homologues, 3-benzoyl-2,7-dimethoxynaphthalene (**I**)[9] and 2,7-dimethoxy-3-(2-naphthoyl)naphthalene (**II**)[10] have been determined by the authors' group (Fig. 1). The determination of the crystal structures of two compounds has highly motived for the authors to complete the probe substance triad for analysis of the effective non-classical hydrogen bonding interactions in crystal by complementation of crystal structural information of the analogous molecule bearing 1-naphthoyl group. Herein, the X-ray crystal structure of the 2,7-dimethoxynaphthalene compound bearing α-naphthoyl group at the 3-position (**1**) is reported (Fig. 2) and the difference in both single molecular crystal structure and crystal packing structure is discussed by comparing with those of the 3-benzoylated and 3-*β*-naphthoylated homologues (**I** and **II**) to clarify the influence and the role of intermolecular noncovalent-bonding interactions in the molecular packing.

Furthermore, the molecular spatial organizations of these compounds in solution are discussed with the aid of NMR spectral method. By this protocol, extraction of the steric factors functioning in determination of the molecular spatial organization is attempted on the basis of comparison of structure in distinct situations with the presence of significant intermolecular noncovalent-bonding interactions in crystal and without nearly absence of intermolecular interactions in solution.

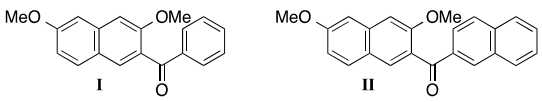


Figure 1. *β*-aroylated naphthalene homologues **I** and **II**.

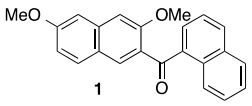


Figure 2. Title compound (**1**).

Experimental

All reagents were of commercial quality and were used as received. Solvents were dried and purified using standard techniques.[11] 2,7-Dimethoxynaphthalene[12] and phosphorus pentoxide–methanesulfonic acid mixture[13] were prepared according to literatures. Synthetic methods and spectral data for *β*-aroylated naphthalene homologues **I** and **II** have been reported in literatures.[9,10]

Measurements

^{1}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_4Si (δ 0.00). ^{13}C NMR spectra were recorded on a JEOL ECX400 spectrometer (100 MHz). Chemical shifts are expressed in ppm relative to internal standard of $CDCl_3$ (δ 77.0). IR spectra were recorded on a JASCO FT/IR-4100 spectrometer (KBr tablet). 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-crystal of title compound **1** was used for data collection on a four-circle Rigaku RAXIS RAPID diffractometer (equipped with a two-dimensional area IP detector). The graphite-monochromated Cu Kα 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 $F^2>2\theta(F^2)$.

Refinement

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* (Rigaku, 1998); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *CrystalStructure* (Rigaku, 2007); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2007)[14]; program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996).[15] The hydrogen bond geometries of title compound **1** are listed in Table 2.

Table 1. Crystallographic data and structure refinement parameters.

Crystal data	
Chemical formula	$C_{23}H_{18}O_3$
M_r	342.37
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	193
a, b, c (Å)	8.8585 (2), 22.1886 (5), 9.10165(19)
β (°)	104.139 (1)
V (Å^3)	1734.80 (7)
Z	4
Radiation type	CuKα
μ (mm^{-1})	0.69
Crystal size (mm)	0.60 × 0.30 × 0.10
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Numerical NUMABS
T_{min}, T_{max}	0.682, 0.934
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30270, 3173, 2587
R_{int}	0.054
(sin θ/λ)max (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $w_R(F^2)$, *S*	0.041, 0.113, 1.09
No. of reflections	3173
No. of parameters	238
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.15

Computer programs: *PROCESS-AUTO* (Rigaku, 1998), *PROCESS-AUTO* (Rigaku, 1998, *CrystalStructure* (Rigaku, 2007), *SIR2004* (Burla *et al.*, 2007), *SHELXL97* (Sheldrick, 2008), *ORTEPIII* (Burnett & Johnson, 1996).

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

D—H···*A*	*D*···*A*
C22–H22C···O3^{i}	3.437(2)
C6–H6···*Cg*^{ii}	3.6749(14)

Symmetry codes: (i) –1+x, 1/2-y, 1/2+z; (ii) 1-x, -y, 1-z. *Cg* is the centroid of the C16–C21 ring.

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

The title compound (**1**) was prepared by treatment of a mixture of 2,7-dimethoxynaphthalene (376 mg, 2.0 mmol) and 1-naphthoic acid (379 mg, 2.2 mmol) with phosphorus pentoxide–methanesulfonic acid mixture (P_2O_5: MsOH = 1: 10 w/w; 4.4 mL). After the reaction mixture was stirred at 333 K for 6 h, the mixture was poured into ice-cooled water and extracted with $CHCl_3$ (15 mL × 3). The combined extracts were washed with 2 M aqueous NaOH (20 mL × 3) followed by washing with brine (20 mL × 3). The organic layer thus obtained was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give a cake (688 mg, quant.). The crude product was purified by flush silica gel chromatography (toluene; yield 64%). Colourless platelet single crystals suitable for X-ray diffraction were obtained by repeated crystallization from $CHCl_3$.

^{1}H NMR δ(400 MHz, $CDCl_3$): 3.73 (3H, s), 3.94 (3H, s), 7.03 (1H, dd, *J* = 2.0, 9.2 Hz), 7.09 (1H, d, *J* = 2.0 Hz), 7.11 (1H, s), 7.43 (1H, t, *J* = 8.0 Hz), 7.53–7.59 (2H, m), 7.62 (1H, d, *J* = 8.0 Hz), 7.67 (1H, d, *J* = 9.2 Hz), 7.91–7.94 (2H, m), 7.99 (1H, d, *J* = 8.0 Hz), 8.60 (1H, d, *J* = 8.0 Hz) ppm. ^{13}C NMR δ (100 MHz, $CDCl_3$): 55.34 (OMe), 55.61 (OMe), 104.86, 105.74, 117.10, 123.05, 124.31, 125.92, 126.26, 127.59, 128.30,128.97, 129.77, 130.40, 130.88, 131.95, 132.16, 133.74, 137.10, 137.73, 156.47 (OAr), 159.67 (OAr), 197.45 (C=O) ppm; IR (KBr): 1660 (C=O), 1628 (Ar), 1503 (Ar), 1250 (C–O–C), 1221 (C–O–C) cm^{-1}. HRMS (FAB; *m*-nitrobenzyl alcohol [*m*-NBA]) m/z: $[M+H]^+$ calcd. for $C_{23}H_{19}O_3$, 343.1334, found, 343.1244. m.p. = 454.8–456.3 K.

Results and Discussion

The single molecular structure of title compound **1** is illustrated in Fig. 3.[16] The interplanar angle between the two naphthalene rings (C1—C10 and C12—C21) is 88.15 (4)°. The dihedral angle between the bridging carbonyl plane [C3—(C11=O1)—C12] and the naphthalene ring of the 2,7-dimethoxynaphthalene core (C1—C10) is larger than that between the bridging carbonyl plane and the naphthalene ring of the 1-naphthoyl group (C12—C21) [65.13 (7)° versus 35.32 (7)°; C4—C3—C11—O1 torsion angle = -61.43 (19)° versus O1—C11—C12—C21 torsion angle = -33.4 (2)°].

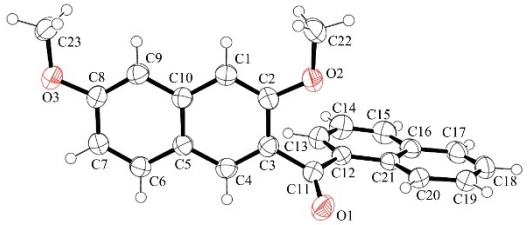
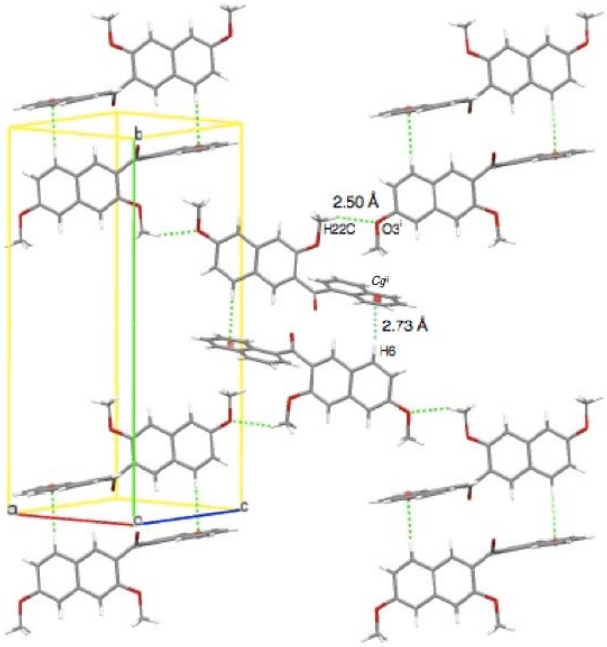


Figure 3. The molecular structure of **1**, with atom numbering. Displacement ellipsoids are drawn at the 50% probability level.

In crystal, dimeric molecular aggregates, each of which is composed of two molecules of title compound **1** nesting inside one another, are two-dimensionally arranged to form a layer (Fig. 4). The layers are piled along *ac* diagonal (Fig. 5). A pair of intermolecular (sp^2)C–H···π hydrogen-bonding interactions between the naphthalene rings of 2,7-dimethoxynaphthalene core and 1-naphthoyl moiety of the counterpart molecule induce the dimeric molecular aggregate (C6–H6···*Cg* = 2.73 Å; *Cg* is the centroid of the C16–C21 ring; symmetry codes: 1 - x, - y, 1 - z; Fig. 4 and Table 2). In addition, four (sp^3)C–H···OCH_3 hydrogen bonds between the methoxy groups link each dimeric molecular aggregate with the four adjacent dimeric molecular aggregates making two-dimensionally accumulated spread structure (C22–H22C···O3 = 2.50 Å; symmetry codes: -1 + x, 1/2 - y, 1/2 + z; Fig. 4, Table 2).

Figure 4. A layer composed of dimeric molecular aggregates in



title compound (**1**), showing (sp^3)C–H…OCH_3 hydrogen bonds and a pair of intermolecular C–H…π hydrogen-bonding interactions. *Cg* is the centroid of the C16–C21 ring [see Table 2 for details; symmetry codes: (i) -1+x, 1/2-y, 1/2+z; (ii)1-x, -y, 1–z].

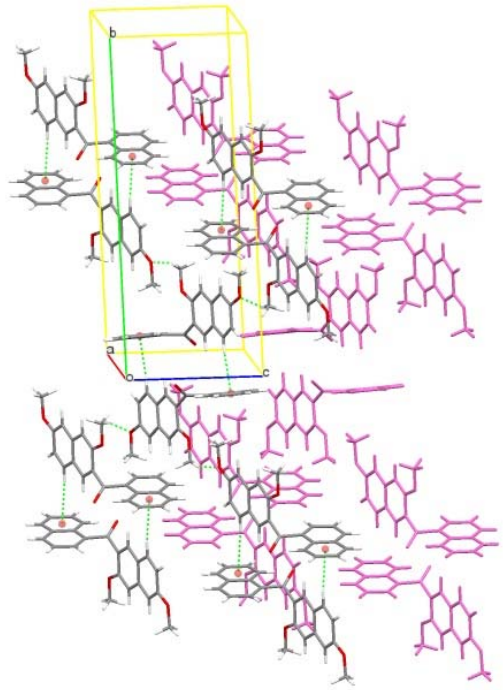
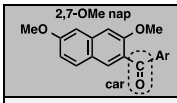


Figure 5. A partial view of the crystal packing of title compound **1**.

There are a lot of reports about dimeric molecular aggregates induced by classical hydrogen bonding interactions such as electronegative-atom-bound hydrogen···electronegative atom bonds.[17] On the other hand, electronegative atom-bound hydrogen···π interactions-induced dimeric molecular aggregates have been reported fewer than the former type of dimeric molecular aggregate.[18] Furthermore, dimeric molecular aggregates induced by van der Waals interactions or C–H…π hydrogen-bonding interactions have been rarely reported. In the crystal of title compound **1**, dimeric molecular aggregates are formed by C–H…π hydrogen bonding interaction. This is one of the most rare cases for such molecular dimeric formation in crystal. It also means that the more effective types of interactions are probably prevented because of substantially immanent intramolecular and intradimeric hindrance of arene moieties.

The crystal structures of two homologous compounds for title compound **1**, *i.e.*, 3-benzoyl-2,7-dimethoxynaphthalene (**I**)[9] and 2,7-dimethoxy-3-(2-naphthoyl)naphthalene (**II**),[10] which have benzoyl group and 2-naphthoyl group at 3-position of the 2,7-dimethoxynaphthalene core respectively in place of 1-naphthoyl group, have been reported recently. Arene ring of aroyl group in these homologous molecules is non-coplanarly located to the 2,7-dimethoxynaphthalene core in the similar fashion for title compound **1**. Table 3 summarizes selected interplanar/dihedral angles of homologues **I**, **II**, and title compound **1**. Interplanar angle between arene rings of aroyl group and 2,7-dimethoxynaphthalene moiety is in the order of homologue **I** [68.32(5)˚] < homologue **II** [78.02(3)˚] < title compound **1** [88.15(4)˚]. The interplanar angle of title compound **1** is rather close to the corresponding interplanar angles in α- and α,α'-positions aroylated naphthalene homologues, *i.e.*, 79.07(4)˚ and 88.19(4)° for 2,7-dimethoxy-1-(1-naphthoyl)naphthalene, which contains two independent molecules in the crystallographic unit-call,[19] and 89.84° and 85.06° for 2,7-dimethoxy-1,8-bis(1-naphthoyl)-naphthalene.[8d] Dihedral angle between the bridged C–(C=O)–C carbonyl plane and the 2,7-dimethoxynaphthalene ring core is in the order of homologue **I** (54.32˚) < title compound **1** [65.13(7)˚] < homologue **II** (70.56˚). Besides, dihedral angle between bridged C–(C=O)–C carbonyl plane and aromatic ring of aroyl group is in the order of homologue **II** (11.53˚) < homologue **I** (21.45˚) < title compound **1** [35.32˚(7)].

Table 3. Selected interplanar/dihedral angles in compound **1** and homologues **I** and **II** (˚).

	**Compound 1**	**Homologue I**	**Homologue II**
2,7-OMe nap and Ar	88.15(4)	68.32(5)	78.02(3)
car...2,7-OMe nap	65.13	54.32	70.56
car…Ar	35.32	21.45	11.53

In the case of title compound **1**, both the 2,7-dimethoxynaphthalene ring core and the aromatic ring of the aroyl group largely deviate from the bridged C–(C=O)–C carbonyl plane, and the deviations are larger than homologue **I**. For homologue **II**, the dihedral angle of the naphthalene core versus the bridging carbonyl plane is the largest and that of aroyl group against the bridging carbonyl plane is the smallest among three compounds. These relative values of interplanar/dihedral angles manifest that title compound **1** has the largest internal steric hindrance among three *β*-aroylated naphthalene compounds.

As described above, title compound **1** affords plane shape alignment as second order accumulation of dimeric aggregates. Contrarily, in crystal of homologue **I**, dimeric molecular aggregates are aligned forming ribbon-like structure. The dimeric molecular aggregate is induced by a pair of intermolecular (sp^2)C–H···O=C hydrogen bonds between the core naphthalene ring and the carbonyl group (C4–H4···O1 = 2.58 Å; symmetry codes: -x+2, -y, -z+1), and is connected with two adjacent dimeric molecular aggregates situated on the opposite side through intermolecular (sp^3)C–H···OCH_3 hydrogen bonds between the methoxy groups (C18–H18B···O3 = 2.42 Å; symmetry codes: x-1, y, z-1), forming ribbon-like structure along *ac* diagonal (Fig. 6, top).

Table 4. Noncovalent-bonßding interactions of title compound **1**, and homologues **I** and **II**.

	Compound 1	**Homologue I**	**Homologue II**
C–H...O hydrogen bonds			
(sp^3)C–H...OCH_3	2.50[i]	2.42[iii]	-
(sp^2)C–H...O=C	-	2.58[iv](pair)	-
C–H...π hydrogen bonding interactions			
(sp^3)C–H...π	-	-	2.80[v]
(sp^2)C–H...π	2.73[ii](pair)	-	-

The C–H…O interactions are elucidated on the basis of shorter distance of two atoms less than the sum of the van der Waals radii.

C–H…π hydrogen bonding interactions are shown in Table when the distance between the H atom and the centroid of the ring is shorter than 3 Å. Symmetry codes: (i) -1+x, 1/2-y, 1/2+z; (ii) 1-x, -y, 1-z; (iii) x-1, y, z-1; (iv) -x+2, -y, -z+1; (v) x, y-1, z.

In the case of homologue **II**, the molecules are directly stacked into columnar alignment along *b* axis (Fig. 6, bottom). The columnar structure is stabilized by intermolecular (sp^3)C–H···π hydrogen-bonding interactions between the methoxy group and the naphthalene ring of the 2-naphthoyl group of the adjacent molecule (C22–H22A···*Cg* = 2.80 Å; symmetry codes: x, y-1, z). The noncovalent-bonding interactions for dimer formation and their alignment in crystals of three homologous compounds discussed above are summarized in Table 4.

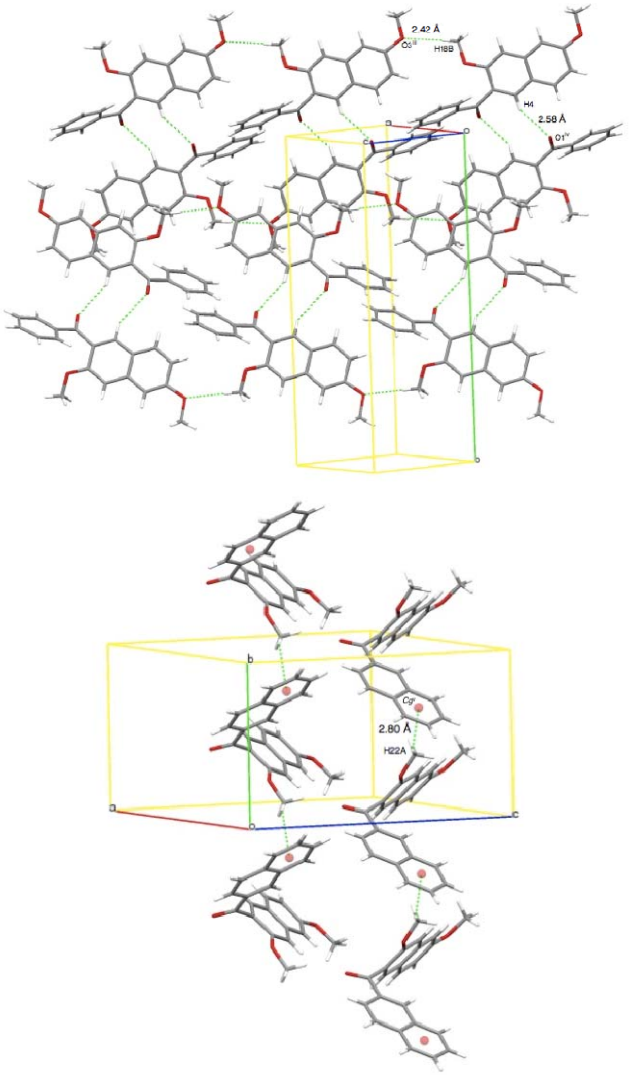


Figure 6. Crystal packing of homologues **I** and **II**: Ribbons composed of dimeric molecular aggregates in homologue **I** [top; see Table 4 for details; symmetry codes: (iii) x-1, y, z-1 (for C18–H18B···O3 hydrogen bonds); (iv) – x+2, –y, –z+1 (for C4–H4···O1 hydrogen bonds)] and column structures induced by C–H···π hydrogen-bonding interactions in homologue **II** [bottom; see Table 3 for details; symmetry codes: (v) x, y-1, z. (for C22–H22A···*Cg* interactions)].

Title compound **1** has deep similarities with both of homologues **I** and **II** in terms of fashion and kind of noncovalent-bonding interactions. Title compound **1** forms a dimeric molecular aggregate as well as homologue **I**. However, higher-order arrangement of dimeric aggregate of title compound **1** and homologue **I** differs distinctively, *i.e.*, title compound **1** forms plane of dimeric aggregates, whereas homologue **I** makes ribbon-like structure of dimers. In both of title compound **1** and homologue **I**, the dimeric molecular aggregates are linked by C–H…O (ethereal oxygen) hydrogen bonding interactions (C–H…OCH_3) between methoxy groups. In crystalline molecular packing of homologue **I**, a dimeric aggregate forms a couple of counter directed (sp^3)C-H…OCH_3 hydrogen bondings with one adjacent dimeric aggregate. The linkages are also formed with another adjacent dimeric aggregate. Accordingly, ribbon structure of homologue **I** through the connection of dimeric aggregates by two couples of (sp^3)C-H…OCH_3 hydrogen bondings is obtained.

The difference in higher-ordered structure between title compound **1** and homologue **I** presumably arises from the spatial organization of respective dimeric molecular aggregates. The dimeric molecular aggregate of title compound **1** is induced by a pair of C–H···π hydrogen-bonding interactions in place of a pair of C–H…O(carbonyl oxygen) hydrogen-bonding ones (C–H…O=C) for homologue **I**. Accordingly, in dimeric molecular aggregate of title compound **1**, naphthalene rings of α-naphthoyl moieties are situated to be faced perpendicularly toward edges of core naphthalene ring of the counter monomer resulting in achieve compact and round shaped aggregate arrangement. On the other hand, for dimeric molecular aggregate of homologue **I** is formed by the non-classical hydrogen bonding interaction between carbonyl oxygen and aromatic hydrogen of the naphthalene core of the counter molecules by rather loose contact, which allows each naphthalene ring of dimeric molecular aggregate to position outer site of aggregate resulting in construction of opened dimeric shape. In the compact shape of the dimeric molecular aggregate of title compound **1**, the 2- or 7-positioned methoxy groups should take the intramolecular position to minimize the steric hindrance in the allowed dimer plane, resulting in alignment of four orientations pointing to the corners of nearly regular-square. Contrarily, the methoxy groups in the dimeric aggregate of homologue **I** take the position on the parallel lines in the rectangular-square shape leading the connection of their edges to form ribbon-like structure.

For crystal of homologue **II**, C–H…π hydrogen-bonding interactions lead to columnar structure. On the basis of above observation, both of C–H···O(ethereal) hydrogen bond and C–H···π hydrogen-bonding interaction are considered as requisites to form two-dimensional molecular network composed of dimeric molecular aggregates. When different interactions of comparative strength present, the predominant interaction might determine the orientation of the relative position of two molecules. If the head-to-tail orientating interaction is predominant, a type of columnar stacking is formed. Otherwise, the head-to-head orientating interaction overcomes, the formation of dimeric aggregate of molecules are precedent. Then, the interaction between dimeric aggregates should determine the most stable alignment under the restriction of inherent steric restriction of the molecule. Accordingly, the spatial organization of the vectors of the effective interactions, *i.e.*, three-dimensional direction, fixes plane- or ribbon-shaped higher ordered accumulation composed of dimeric molecular aggregates. Consequently, either C–H···π hydrogen-bonding interaction

or C–H···O(ethereal) hydrogen bond as the predominant interaction probably leads one-dimensional molecular arrangements such as columnar structure. As described above, title compound **1** plausibly has largest internal steric repulsion among three *β*-aroylated homologous compounds. The internal steric repulsion seems to interfere formation of superior intradimer and interdimer interactions for dimer to align on the parallel direction such as C–H···O(ethereal) hydrogen bonds that effectively function between dimeric aggregates of homologue **I**. Consequently, cooperation of two couples of intermolecular interactions with counter orientation and same strength functioning between dimeric molecular aggregates most effectively forms two-dimensionally spread arrangement when the interactions are oriented in the perpendicular directions. To the contrary, lack of either of interactions strongly leads unidirectional connection of molecules such as columnar or ribbon structure instead two-dimensional arrangement hardly forms.

In a natural sequence of the structural study on title compound **1** and the homologues **I** and **II**, the molecular spatial organization of these compounds in solution have been investigated referring the results of X-ray crystal analysis. Fig. 7 exhibits ^{1}H NMR spectra of the methoxy (δ 3.6~4.0 ppm) and aromatiçδ 6.0~9.0 ppm) regions for title compound **1** and the homologous compounds **I** and **II**. The signals assigned to the 2- and 7-methoxy groups of the 2,7-dimethoxynaphthalene core in homologues **I** and **II** are observed at almost the same chemical shifts, respectively. In the case of title compound **1**, the signals assigned as the proton of the 2-methoxy group are shifted to higher magnetic field than other two homologues. Ahead of comparison of chemical shift in the aromatic protons for homologues **I** and **II**, regional equivalency of the related protons sliding the three homologues are organized. In addition to the apparent equivalency for each proton on 2,7-dimethoxynaphthalene core such as those of 1- and 4-positions on three homologous compounds (**e** and **a**), the protons of 1(3)- and 4-positions in 2-naphthoyl group [**f'** (**f**) and **g**] of homologue **II** are fixed to correspond to protons of 2(6)- and 3(5)-positions of the benzoyl group (**f** and **g**) in homologue **I**, respectively. From the standpoint of proton equivalency or proton correspondence among these homologous molecules, the corresponding signals of these common protons in homologue **II** are found essentially shifted to lower magnetic field than homologue **I**.

In the case of title compound **1,** the protons on 1- and 4-positions of the 2,7-dimethoxy-naphthalene moiety (**e** and **a**) and 2- and 3-positions of the 1-naphthoyl group (**f** and **g**) are common with two homologues. For one common proton (**a**) in the 2,7-dimethoxynaphthalene core, the signal is shifted slightly to lower magnetic field than homologues **I** and **II**, whereas the signal of the other common proton (**e**) is almost same with the two homologues. The signal of the 3-position of the 1-naphthoyl group (**g**) is intermediately situated between two homologues. On the other hand, the signal of the proton of the 2-position of the 1-naphthoyl group (**f**) of title compound **1** is shifted more largely to lower magnetic field than other two homologues. For natural extension of consideration of chemical shifts of the corresponding protons in benzoyl, ι-naphthoyl, and □-naphthoyl groups, as the *β*-aroyl groups in homologue **I**, title compound **1**, and homologue **II**, the normalized or roughly assessed virtual chemical shifts are compared with the experimentally observed chemical shifts for these protons.

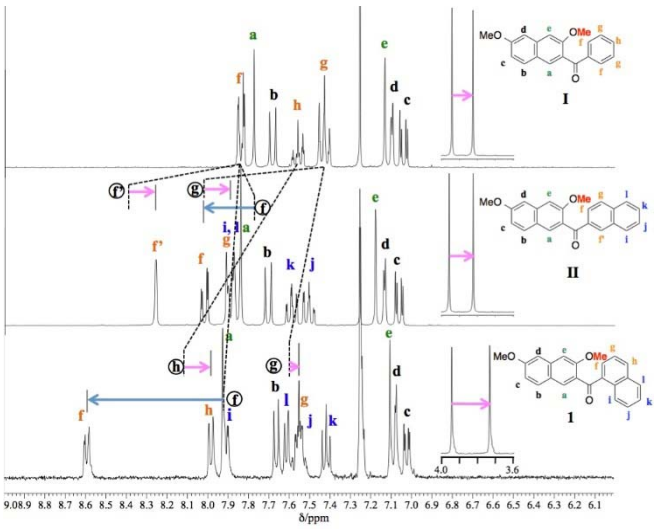
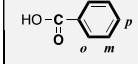
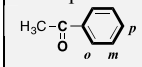
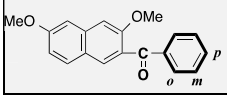


Figure 7. ^{1}H NMR spectra in $CDCl_3$ at r.t (300 MHz) : Homologue **I** (top), homologue **II** (middle), and compound **1** (bottom). Dotted-lines on the charts with circled alphabetical denotations display the positions of estimated signals for protons corresponding to the same alphabetical denotations. The estimated chemical shifts are listed in Table 7, which are determined according to the method described in the note of Tables 7, 6, and 5.

First, comparison of chemical shifts of protons in phenyl groups of homologue **I** with those of analogous arenecarbonyl compounds has been undertaken. Table 5 shows the chemical shifts of protons of benzoyl groups in ^{1}H NMR spectra of homologue **I**, acetophenone, and benzoic acid. Table 5 also displays difference in chemical shift among *o*-, *m*-, and *p*-positioned protons on individual benzoyl groups. The chemical shifts for *o*-, *m*-, and *p*-protons in three compounds are observed in the range of 7.84–8.12 ppm (0.28), 7.41–7.45 ppm (0.04), and 7.56–7.62 ppm (0.06), respectively. The values in the parentheses are the ranges of the chemical shift distribution for the protons of the corresponding positions. Furthermore, the difference in chemical shifts between two protons of the same molecules are found in the ranges of -0.41 to -0.67 (0.26) for *m*- against *o*-, +0.13 to +0.17 (0.04) for *p*- against *m*-, and -0.28 to -0.50 (0.22) for *p*- against *o*-positions, respectively. The deviations in chemical shift among three aromatic protons of homologue **I** (designated as **f**, **g**, and **h**) show good accordance with those observed among the corresponding protons of benzoic acid and acetophenone. These data suggest that the ^{1}H NMR spectra of benzoyl groups of homologue **I**, acetophenone, and benzoic acid show essentially same spectral patterns, meaning that spatial organization of benzoyl group of homologue **I** has rather conventional structural-hindrance situation as such a type of aromatic ketone and carboxylic acid molecules without specified steric effect.

On the analogy of above consideration, the virtual chemical shifts of protons of α- and *β*-naphthoyl groups (**f**, **g**, and **f'**) have been estimated in order to compare the observed values with for elucidation of unusual deviation of the chemical shifts of these compounds.

Table 5. Chemical shifts and their differences of the protons on benzoyl groups of benzoic acid, acetophenone and homologue **I**

	Positions	Chem. shifts	Δδ(*m-o*)[b] Δδ(*p-m*)[b]	Δδ(*p-o*)[b]
Benzoic acid[a] 	*o-*	8.12	-0.67	-0.50
	m-	7.45	+0.17	
	p-	7.62		
Acetophenone[a] 	*o-*	7.89	-0.48	-0.33
	m-	7.41	+0.15	
	p-	7.56		
Homologue **I** 	*o-*	7.84	-0.41	-0.28
	m-	7.43	+0.13	
	p-	7.56		
		/ppm	/ppm	/ppm

[a] Chemical shifts of benzoic acid and acetophenone are referred to the Spectral Data Base (SDBS) provided by National Institute of Advanced Industrial Science and technology (AIST), in $CDCl_3$. [b] Δδ's are calculated by subtraction of the reference chemical shift of the signals for individual protons from those of designated protons.

Deviation values from the estimated value in chemical shifts among these protons are calculated referring to those of the corresponding arenecarboxylic acid (Fig. 8 and Table 6). The observed values and the deviation are displayed in Table 7 (Fig. 9). That is, employing the deviation values for the corresponding arenecarboxylic acids from benzoic acid shown in Table 6, the chemical shifts for protons of homologue **II** and title compound **1** are estimated on the basis of the chemical shifts of homologue **I** and tabulated in Table 7. The estimation was performed as follows: the virtual chemical shifts of protons of 2,7-dimethoxy-3-(1-naphthoyl)naphthalene (title compound **1**) and homologue **II** were calculated by adding/drawing the corresponding deviation values determined for α- and *β*-naphthoic acids against benzoic acid and listed in Table 6 [α-naphthoic acid: +0.08 (**f**), +0.17 (**g**), +0.56 (**h**); *β*-naphthoic acid: -0.07 (**f**), +0.59 (**g**), +0.55 (**f'**)] to/from the observed chemical shifts for homologue **I**, 3-benzoyl-2,7-dimethoxynaphthalene.

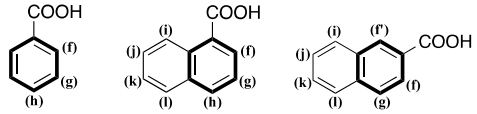


Figure 8. Designation of protons on benzoic acid, α-naphthoic acid and *β*-naphthoic acid

In Fig. 7, the several virtual chemical shifts are inserted for the selected aromatic protons of title compound **1** and homologue **II** as a vertical dot-line with circled **f**, **g**, **f'**, and **h** designations, which are estimated on the basis of the chemical shifts for protons of homologue **I** and relationship among chemical shifts for protons of α-naphthoic acid and *β*-naphthoic acid versus those of benzoic acid as the reference compound with homologue **I** (Table 6 and Table 7). The comparison between the observed chemical shifts and the estimated ones obtained according to above mentioned manipulation shows that there are characteristic magnetic field shifts of observed chemical shift values for protons on the carbons adjacent to and near the carbonyl-substituted carbon.

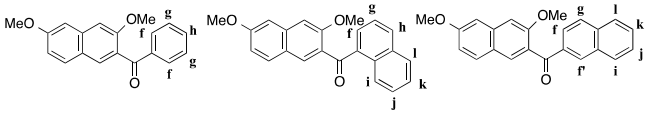


Figure 9. Designation of protons on title compound **1** and homologues **I**/**II**

Especially, the observed chemical shift of the 2-positioned proton of the 1-naphthoyl group of title compound **1** (**f**, δ 8.60 ppm) shows the largest deviation compared to the estimated value (δ 7.92 ppm). And about 3-positioned proton on the 1-naphthoyl group of title compound **1** (**g**), the observed value (δ 7.56 ppm) and the estimated one (δ 7.60 ppm) are almost same. On the other hand, the observed chemical shift of the 3-positioned proton of 2-naphthoyl group (**f**, δ 8.02 ppm) in homologue **II** deviates from the estimated one (δ 7.77 ppm) on a same direction toward lower magnetic field as well as proton (**f**) in title compound **1**, however the deviation magnitude is medium. At the same time, the observed chemical shift of 1-positioned proton of 2-naphthoyl group (**f'**, δ 8.26 ppm) in homologue **II** has found to deviate on the opposite direction with a moderate magnitude compared to the estimated value (δ 8.39 ppm) toward higher magnetic field. Totally, deviation on observed chemical shift of the 1- and 3-positioned protons (**f** and **f'**) from the estimated values for homologue **II** is almost equalized, whereas the deviation between observed chemical shift and estimated one for proton (**f**) in title compound **1** is emphasized apparently. In title compound **1**, the deviation of observed chemical shift from estimated one for 2-positioned proton (**f**) is apparently emphasized against small deviation for 3-positioned proton (**g**).

Table 6. Chemical shifts of the protons on aroyl group of benzoic acid, α-naphthoic acid and β-naphthoic acid with deviation of the shifts from the corresponding protons of benzoic acid

Acid	Chemical shift/ppm							
	f	**g**	**h**	**f'**	**i**	**j**	**k**	**l**
Benzoic[a]	8.12	7.45	7.62	8.12	-	-	-	-
α-naphthoic	8.20	7.62	8.18	-	8.93	7.68	7.61	8.04
[deviation][b]	+0.08	+0.17	+0.56					
β-naphthoic[a]	8.05	8.04	-	8.67	8.15	7.64	7.68	8.03
[deviation][b]	-0.07	+0.59	-	+0.55				

[a] Chemical shifts of benzoic acid and acetophenone are referred to the Spectral Data Base (SDBS) provided by National Institute of Advanced Industrial Science and technology (AIST), in DMSO-d_6. [b] Deviation value is calculated by subtraction of the chemical shift of signals for individual protons on benzoic acid from the chemical shift of the corresponding protons on α- or β-naphthoic acids.

This observation displays that the deshielding effect against homologue **II** is almost equalized on 1- and 3-positioned protons (**f** and **f'**), whereas the deshielding effect is applied with distinctive disproportionation on 2- and 3-positioned protons (**f** and **g**) for title compound **1**

Table 7. Observed and estimated chemical shifts of the selected protons of title compound **1** and homologues **I**/**II** with deviation between observed and estimated values.

	Chemical shift/ppm			
	f	**g**	**h**	**f'**
Benzoylated naphthalene **I**	7.84	7.43	7.56	7.84
α-naphthoylated **1** (observed)	8.60	7.56	7.99	
(*estimated*)	*7.92*	*7.60*	*8.12*	
[deviation][a)]	[+0.68	-0.04	-0.13]	
β-naphthoylated **II** (observed)	8.02	7.90	-	8.26
(*estimated*)	*7.77*	*8.03*	-	*8.39*
[deviation] [a)]	[+0.25	-0.12	-	-0.13]

[a)] Deviation for the protons from the corresponding protons of homologue **I**. "(Estimated) chemical shift values" are calculated by addition/subtraction of the deviation values between α/β-naphthoic acid and benzoic acid tabulated in Table to/from the observed chemical shift of the signal for individual protons on title compound **1** (α-naphthoylated compound **1**) or homologue **II** (β-naphthoylated homologue **II**). "[Deviation] values" are calculated by subtractionof the estimated chemical shift of the signal for individual protons from those of the corresponding observed chemical shifts.

The unbalanced deviation magnitudes of chemical shifts of signals along with opposition of direction observed in title compound **1** indicate that these protons are distinctively influenced by different magnetic field effect. The large lower magnetic field deviation of the proton (**f**) of carbonyl adjacent position on 1-naphthoyl group in title compound **1** is considered due to the efficient deshielding effect of the opposing induced magnetic field. On the other hand, the good coincidence between the observed and the estimated chemical shifts for 3-positioned proton (**g**) on 1-naphthoyl group of title compound **1** means that the proton receives almost no effect or compensated effects originated from congestedly accumulated aromatic ring moieties. From the viewpoint of function of induced magnetic field arising from circuit current on the aromatic ring, the proton (**f**) receiving opposing magnetic field more strongly is interpreted to situate in near spatial position against the effective aromatic rings for longer time. This supposed spatial alignment should mean the congested and hindered spatial organization of arene rings to each other resulting in almost perpendicular position of two naphthalene rings. These restrictions lead the conformation more fixed with contact relation of arene rings with only a small space for conformational perturbation. In addition, the highly crowded spatial situation of α-naphthoyl connection might support fixation of α-naphthyl–carbonyl–β-naphthyl bonding in title compound **1**. Contrarily, the two naphthalene rings in homologue **I** have enough room to take various conformations around ketonic carbonyl bonding. It plausibly affords almost equal average distances between individual aromatic protons and the adjacent naphthalene ring, which leads moderate deviation to lower in chemical shift for homologue **I**.

Furthermore, orientation of methoxy group at 2-position of the 2,7-dimethoxynaphthalene moiety is also fixed loosely by steric hindrance of 1-naphthoyl group in title compound **1**. In consequence of this, the signal ascribed to the methoxy group at the 2-position of the 2,7-dimethoxynaphthalene is shifted to higher magnetic field by the local magnetic field induced from circulating ring current of 2,7-dimethoxynaphthalene core, which opposes the external magnetic field. On the other hand, homologues **I** and **II** rather smoothly undergo interconversion among rotational isomers with the rather lower barrier. Under these circumstances, the induced magnetic field effect that functions distinctly in title compound **1** is in turn largely depressed in homologues **I** and **II**. Furthermore, signals of title compound **1** are observed influenced by clearly different magnetic field effects. These results strongly indicate that conformational flexibility of title molecule **1** is lower than the two homologous molecules. Consequently, degree of fixation of conformation is decreased in an order of title compound **1**, homologue **II**, and homologue **I** (Figure 10). These interpretations are supported by rather good agreement with estimation of internal steric hindrance elucidated on the basis of X-ray crystal structure analyses.

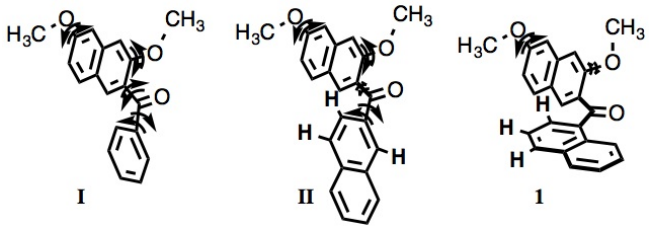


Figure 10. Plausible spatial organization in solution: homologue **I** (left), homologue **II** (middle), and compound **1** (right).

Conclusion

Crystal structure of 3-(1-naphthoyl)-2,7-dimethoxynaphthalene has been determined. In the crystal packing, the molecules are arranged in a layer composed of the dimeric molecular aggregates. Systematic comparison of single molecular structure and molecular packing with noncovalent-bonding interactions for three homologous β-aroylated naphthalene compounds has revealed correlation of single molecular and molecular packing structure motif in crystal and effective non-classical hydrogen-bonding interactions. Both C–H…O=C hydrogen bond and C–H…π hydrogen bonding interactions of comparable magnitude and suitable spatial orientation are required to form two-dimensional molecular packing motif. To perform planarly alignment of molecules, formation of dimeric aggregate of *C2* symmetry having two couples of functional groups, methoxy groups, in the regular-squarely oriented directions is significant. In title compound **1**, two methoxy groups of 2,7-dimethoxynaphthalene core as donating role groups in (sp^3)C–H…O(ethereal) hydrogen bonding interaction and the other two methoxy groups as acceptors are situated perpendicularly in regular-square directions enabling functioning of four identical interactions along four directions toward the four corners of regular-square plane.

Lack of either of the presence of the predominant effectiveness of non-symmetric interaction induces one-dimensional molecular packing motif such as ribbon or columnar structure.

To stabilize the molecular packing in the crystal on condition that the single molecular structure is of conformationally fixed spatial organization of aromatic rings accumulation without coplanarity, the title molecules are arranged to enable cooperative contribution of larger number of moderately effective non-classical hydrogen bonding interactions in crystal being performed. In addition, intramolecular steric hindrance should oblige title compound **1** to take conformationally fixed single molecular spatial organization. As a result, cumulatively noncovalent-bonding interactions, especially two or more kinds of non-classical hydrogen bonding interactions, are only allowed to function on perpendicular directions not on the same a parallel direction, resulting in stabilization by dimer aggregation and formation of layers composed of the regular-squarely arranged dimeric molecular aggregates for title compound **1**.

In ^{1}H NMR study, signals of title compound **1** influenced by distinctively different magnetic field effect are observed. These results strongly indicate that conformational flexibility of title molecule **1** is lower than the two homologous molecules. The result indicates that origin of deshielding effect is essentially identical, however the degree against individual protons is different between title compound **1** and homologue **II**. In the case of homologue **II**, induced magnetic field arising from circuit current on 2,7-dimethoxynaphthalene ring core is distributed into two protons (**f** and **f'**) at 1- and 3- positions of the 2-naphthoyl group with comparative magnitude but on opposite directions when observed chemical shifts are compared to the estimated ones.

On the other hand, the induced magnetic field influences apparently into only 2-positioned proton (**f**) of 1-naphthoyl group in title compound **1**. This implicitly leads us to the conclusion that the naphthalene ring of 2-naphthoyl group in homologue **II** is considered loosely fixed to the 2,7-dimethoxynaphthalene ring and swaying, whereas that of 1-naphthoyl group in title compound **1** plausibly is almost fixed in some perpendicular fashion against the 2,7-dimethoxynaphthalene ring. Naturally, the 2-positioned methoxy group of the 2,7-dimethoxynaphthalene ring in title compound **1** might be influenced strongly by induced magnetic field arising from circuit current on the fixed 1-naphthoyl group. The concluded relative degree of fixation of conformation derived from ^{1}H NMR analyses show good agreement with elucidated characteristics of crystal structures.

Spatial organizations of these compounds in crystal and in solution are commonly interpreted from the point of intermolecular steric hindrance of individual compounds that determines the molecular conformational flexibility and potential for formation of effective non-classical hydrogen bonding interactions.

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