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# Crystal structure of 1-benzoyl-2,7-dimethoxy-8-(3,5-dimethylbenzoyl) naphthalene: Head-to-head fashioned molecular motif for accumulating weak non-classical hydrogen bonds

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## ABSTRACT

Title compound, 1-benzoyl-2,7-dimethoxy-8-(3,5-dimethylbenzoyl)naphthalene, an unsymmetrically substituted aromatic diketone compound having non-coplanarly accumulated aromatic rings structure, has been synthesized and its crystal structure has been determined by X-ray crystallography. The asymmetric unit of title compound contains two independent conformers. For each conformer, the two aroyl groups are non-coplanarly situated against the naphthalene ring plane and oriented in an opposite direction. The 3,5-dimethylbenzoyl group leans more than the non-substituted benzoyl group on the other *peri*-position of the naphthalene ring. The characteristics in the single molecular crystal structure of this unsymmetrical compound show unique relationship with two symmetrically substituted homologues, namely 1,8-dibenzoyl-2,7-dimethoxynaphthalene and 2,7-dimethoxy-1,8-bis(3,5-dimethylbenzoyl) naphthalene. Dihedral angles between 3,5-dimethylbenzene ring and naphthalene ring of 2,7-dimethoxy-1,8-bis(3,5-dimethylbenzoyl)naphthalene are larger than those between benzene ring and naphthalene ring of 1,8-dibenzoyl-2,7-dimethoxynaphthalene. Dihedral angle between 3,5-dimethylbenzoyl group and naphthalene ring in title compound is close to those of symmetrical homologue having two 3,5-dimethylbenzoyl groups. In the similar manner, dihedral angle between non-substituted benzoyl group and naphthalene ring in title compound is also close to those of symmetrical homologue bearing two non-substituted benzoyl groups. On the other hand, the crystal packing of title compound has rather similar feature with 2,7-dimethoxy-1,8-bis(3,5-dimethylbenzoyl)naphthalene. Two compounds have common crystalline molecular structural motif of head-to-head fashioned intermolecular interaction of 3,5-dimethylbenzoyl moieties. It is interpreted that the interactions between (sp$^3$)C–H and π orbital preferentially govern the molecular packing motif. Molecular structure feature of title compound and the symmetrically 3,5-dimethylbenzoylated homologue strongly manifests that accumulation of weak non-classical hydrogen bonds play a crucial role in determination of the crystal packing rather than sole function of stronger non-classical hydrogen bond and π...π stacking.

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## 1. Introduction

With the accelerated accumulation of X-ray crystallographical analyses of organic compounds for these decades, non-covalent bonding interactions [1,2] have gained expanding recognition as one of governing factors concerning determination of spatial organization of organic molecular crystals [3-5]. As a natural consequence, the standpoint has been promoting the new chemistry area of accumulated molecules, for example, crystal engineering of supramolecular assembly and supramolecular architecture [6-9]. Classical hydrogen bonds and π...π stacking interactions have been regarded to play an decisive role in crystal structural motif and have been investigated in detail for a long time [10-16], whereas the studies of next weaker non-covalent bonding interaction, such as non-classical hydrogen bonds where C–H group acts as hydrogen donors, have received attention as object for semi-quantitative investigation only for the last two decades [17-19]. In principle, all organic molecules have alkyl groups and/or aromatic rings, therefore universal understanding of non-classical hydrogen bonds containing (sp$^2$)C–H bonds or (sp$^3$)C–H ones is surely of great value. One of efficient approaches for this purpose is the study of reliable homologous and/or analogous compounds that can be analyzed hierarchically to reveal the relationship among molecular structure, non-classical hydrogen bonds and molecular accumulation alignment. The authors have reported single molecular structures and the structural features of the molecular packings for roughly ninety compounds having 1,8-diaroylated naphthalene skeleton or the homologous/analogous structure *via* the Cambridge Structure Database (CSD) [20-26]. Molecular structures of 1,8-diaroylated 2,7-dialkoxynaphthalene compounds in crystal solid state have common features of two aroyl groups being non-coplanarly located to the 2,7-dialkoxynaphthalene plane and usually oriented in an opposite direction accompanying with a few exceptional compounds bearing unidirectional-alignment of aroyl groups. The molecular packing of 1,8-diaroylated 2,7-dialkoxynaphthalene compounds are mainly stabilized by weak non-covalent-bonding interactions. Three kinds of

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

| | |
|---|---|
| *Crystal data* | |
| Chemical formula | $C_{28}H_{24}O_4$ |
| $M_r$ | 424.50 |
| Crystal shape, colour | Block, colourless |
| Crystal system, space group | Triclinic, *P*-1 |
| Temperature (K) | 193 |
| *a*, *b*, *c* (Å) | 8.30720(15), 15.2286 (3), 18.1704 (4) |
| β (°) | 84.5870(10) |
| V (Å$^3$) | 2173.50(7) |
| Z | 4 |
| Radiation type | Cu Kα |
| μ (mm$^{-1}$) | 0.69 |
| Crystal size (mm) | 0.30 ×15× 0.05 |
| *Data collection* | |
| Diffractometer | Rigaku R-AXIS RAPID diffractometer |
| Absorption correction | Numerical NUMABS |
| $T_{\min}$, $T_{\max}$ | 0.856, 0.966 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 41236, 7836, 6258 |
| $R_{int}$ | 0.026 |
| (sin θ/λ)max (Å$^{-1}$) | 0.602 |
| *Refinement* | |
| R[$F^2$ > 2σ($F^2$)], wR($F^2$), S | 0.042, 0.127, 1.10 |
| No. of reflections | 7836 |
| No. of parameters | 577 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e.Å$^{-3}$) | 0.35, -0.36 |
| CCDC no. | 1541862 |

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).

non-classical hydrogen bonds, (sp$^2$)C–H···O=C hydrogen bond, (sp$^3$)C–H···O hydrogen bond, and C–H···π hydrogen-bonding interaction, and π···π stacking interaction are observed in decreasing order of frequency in the crystals of the 1,8-diaroylated naphthalene compounds and homologues/ analogues. These features can be interpreted that the non-coplanarly accumulated aromatic rings structure naturally disturbs formation of efficient and strong interactions of π…π stacking. Under these circumstances, the authors planned to elucidate the fundamental role of non-classical hydrogen bonds, *i.e.*, weak hydrogen bonds between C–H group and electron rich atom/group in crystal structure determination by the aid of structure analysis of systematically designed 1,8-diaroylated naphthalene compounds. Herein, crystal structure of 1-benzoyl-2,7-dimethoxy-8-(3,5-dimethylbenzoyl)naphthalene is demonstrated. The compound has characteristic molecular structure possessing two different aroyl groups at *peri*-positions (1,8-positions) of the naphthalene ring. The crystal structure is discussed from the standpoint of clarifycation of the correlation among single molecular structure, non-classical hydrogen bonds and molecular packing structure through comparison with the symmetrically substituted homologous compounds, 1,8-dibenzoyl-2,7-dimethoxynaphthalene [25] and 2,7-dimethoxy-1,8-bis(3,5-dimethylbenzoyl) naphthalene [26]. From the viewpoint of molecular structure, title compound is recognized as a wedding structure of two symmetric homologous compounds. Therefore, title compound is expected to give discriminative information about the role of type and position of substituents on the aroyl group in spatial organization.

## 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 [27]. Synthetic methods and spectral data for 1-benzoyl-2,7-dimethoxynaphthalene [28] have been reported in literature.

### 2.2. Measurements

$^1$H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (300 MHz). Chemical shifts are expressed in ppm relative to internal standard of $Me_4Si$ (δ 0.00 ppm). $^{13}$C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (75 MHz). Chemical shifts are expressed in ppm relative to internal standard of $CDCl_3$ (δ 77.0 ppm). 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.

### 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 monochromated 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 $F^2$>2σ ($F^2$).

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* [29]; cell refinement: *PROCESS-AUTO* [29]; data reduction: *CrystalStructure* [30]; program(s) used to solve structure: *SIR2004* [31]; program(s) used to refine structure: *SHELXL97* [32]; molecular graphics: *ORTEPIII* [33]. The hydrogen bond geometries of title compound are listed in Table 2.

### 2.4. Synthesis of title compound

To a 10 mL flask, 3,5-dimethylbenzoyl chloride (0.60 mmol, 101 mg), titanium chloride (2.7 mmol, 240 mg) and methylene chloride (0.75 mL) were placed and stirred at room temperature. To the reaction mixture thus obtained 1-benzoyl-2,7-dimethoxynaphthalene (0.30 mmol, 88 mg) was added. After the reaction mixture was stirred at room temperature for 24 h, it was poured into ice-cold water (30 mL). The aqueous layer was extracted with $CHCl_3$ (20 mL × 3). The combined

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

| | *D–H* | *H···A* | *D...A* | *D*—H···*A* |
|---|---|---|---|---|
| C39–H39B...O4 $^{i}$ | 0.98 | 2.401 | 3.227(2) | 142 |
| C40–H40C...O7 $^{ii}$ | 0.98 | 2.325 | 3.295(2) | 170 |
| C34–H34...O7 $^{ii}$ | 0.95 | 2.677 | 3.257(2) | 120 |
| C11–H11A...O8 $^{iii}$ | 0.98 | 2.702 | 3.342(3) | 123 |
| C56–H56...O1$^{iv}$ | 0.95 | 2.713 | 3.476(3) | 138 |
| C11–H11C...Cg $^{v}$ | 0.98 | 2.988 | 3.378(2) | 105 |
| C15–H15...Cg $^{vi}$ | 0.95 | 2.940 | 3.8586(18) | 163 |
| C21–H21C...Cg $^{vii}$ | 0.98 | 2.960 | 3.747(2) | 138 |
| C31–H31...Cg $^{viii}$ | 0.95 | 2.846 | 3.774(2) | 166 |

* Symmetry codes: (i) -1+*x*, *y*, z; (ii) 1-*x*, -*y*, 1-*z*; (iii) *x*, 1+*y*, *z*; (iv) *x*, -1+*y*, *z*; (v) 1-*x*, 1-*y*, 1–*z*; (vi) 1+*x*, *y*, *z*; (vii) *x*, *y*, *z*; (viii) 1-*x*, -*y*, 1-*z*.

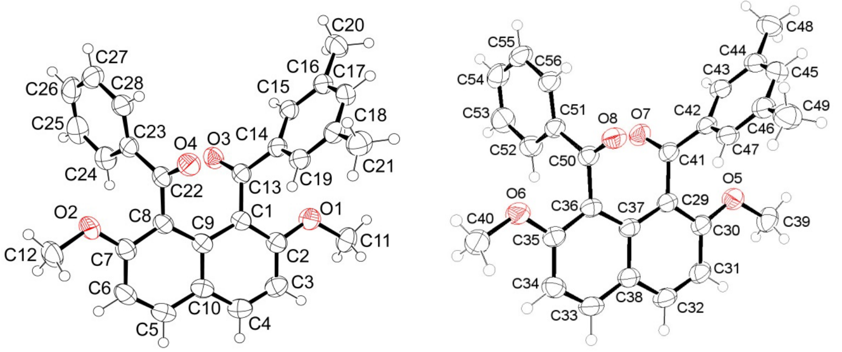

**Figure 1.** Molecular structures of conformers (G, left) and (B, right) with displacement ellipsoids at 50% probability.

extracts were washed with 2 M aqueous NaOH followed by washing with brine. The organic layers thus obtained were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give cake. The target product was isolated by reprecipitation from hexane and $CHCl_3$. Colorless platelet single crystals suitable for X-ray crystallography were obtained by crystallization from acetonitrile (isolated yield 83%, colourless, melting point 491-492 K).

*1-Benzoyl-2,7-dimethoxy-8-(3,5-dimethylbenzoyl)naphthalene*: Color: Colourless. Yield: 83%. M.p.: 491-492 K. IR (KBr, ν, cm$^{-1}$): 1662 (C=O) (ketone), 1609 (Ar), 1560 (Ar), 1511 (Ar), 1267 (Ar-O-$CH_3$), 1040 (ArC-O-$CH_3$). $^1$H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.24 (s, 6H, $CH_3$), 3.65 (s, 3H, $OCH_3$), 3.67 (s, 3H, $OCH_3$), 7.05 (s, 1H, Ph-H), 7.18 (d, *J* = 9.0 Hz, 1H, naphthalene-H), 7.19 (d, *J* = 9.0 Hz, 1H, naphthalene-H), 7.28 (s, 2H, Ph-H), 7.31 (t, *J* = 7.5 Hz, 2H, Ph-H), 7.44 (t, *J* = 7.5 Hz, 1H, Ph-H), 7.67 (d, *J* = 7.5 Hz, 2H, Ph-H), 7.90 (d, *J* = 9.0 Hz, 1H, naphthalene-H), 7.93 (d, *J* = 9.0 Hz, 1H, naphthalene-H). $^{13}$C NMR (75 MHz, $CDCl_3$, δ, ppm): 197.270 (1C, *C*=O), 196.897 (1C, *C*=O), 156.456 (1C, Ar-*C*-OMe), 156.389 (1C, Ar-*C*-OMe), 138.730 (1C, Ar-*C*), 137.444 (1C, Ar-*C*), 134.825 (2C, Ar-*C*), 132.678 (1C, Ar-*C*), 132.210 (2C, Ar-*C*), 132.047 (2C, Ar-*C*), 129.882 (2C, Ar-*C*), 129.189 (1C, Ar-*C*), 128.108 (1C, Ar-*C*), 127.908 (1C, Ar-*C*), 127.152 (1C, Ar-*C*), 125.642 (1C, Ar-*C*), 121.989 (1C, Ar-*C*), 121.502 (1C, Ar-*C*), 111.578 (1C, Ar-*C*), 111.272 (1C, Ar-*C*), 56.662 (1C, O*C*$H_3$), 54.490 (1C, O*C*$H_3$), 21.326 (2C, *C*$H_3$). HR-MS (FAB; *m*-NBA, *m/z*, $[M+H]^+$, Calcd. for $C_{28}H_{25}O_4$, 425.1753; found, 425.1754.

## 3. Results and discussion

The asymmetric unit of title compound contains two independent conformers labelled (G) and (B) (Figure 1). Between two conformers, there are apparently scarce differences observed in spatial organization. The two aroyl groups are non-coplanarly situated to the naphthalene ring plane and they are oriented in an opposite direction. The 3,5-dimethyl benzoyl group leans more than the non-substituted benzoyl group in the same molecule. The interplanar angles between phenyl ring and naphthalene ring and those between two kinds of phenyl rings are distinctly different for two conformers. The interplanar angles between the best planes of the benzene ring and the naphthalene ring are 71.15° for conformer (G) and 75.61° for conformer (B), respectively. Furthermore, the interplanar angles between the best planes of the 3,5-dimethylbenzene ring and the naphthalene ring are 79.93° for conformer (G) and 87.95° for conformer (B). The two interplanar angles of conformer (B) described above are larger than those of conformer (G), however interplanar angles between the phenyl rings are almost the same for both conformers, *i.e.*, 51.48° for conformer (G) and 51.26° for conformer (B). These structural features indicate that the 3,5-dimethylbenzene ring of conformer (B) is more twisted against the carbonyl moiety than conformer (G). The torsion angles between the 3,5-dimethylbenzene ring and the carbonyl moiety are 145.05° for conformer (B) and 152.56° for conformer (G), respectively. In the crystal packing of title compound, each conformer exhibits axial chirality with either *R,R*- or *S,S*-stereogenic axis. Therefore, the asymmetric unit cell contains one enantiomeric pair for each conformer. *R,R*-enantiomer of conformer (G) is engaged with *R,R*-enantiomer of conformer (B) in head-to-head fashion overlapping 3,5-dimethylbenzene rings and *vice versa*, *S,S*-enantiomer of conformer (B) with *S,S*-enantiomer of conformer (G) (Figure 2). In the rectangular-shaped tetrameric conformer aggregate thus formed, *R,R*-isomer of conformer (*R*-B), *S,S*-isomer of conformer (*S*-G), *S,S*-isomer of conformer (*S*-B) and *R,R*-isomer of conformer (*R*-G) are circularly linked parallel to *bc*-plane through weak non-classical hydrogen bonds of {*R**-G}(7-methoxy)C–H...π(3,5-dimethylbenzene){*S**-B} hydrogen bonds [C11–H11C...Cg = 2.99 Å; Cg = C42–C47 ring], {*S**-B}(benzoyl)C–H$_{(o-)}$...O(7-methoxy){*R**-G} [C56–H56...O1 = 2.71 Å], {*R**-G}(7-methoxy)C–H...O=C(benzoyl){*S**-B} [C11–H11A...O8 = 2.70 Å] and {*R**-G}(methyl)C–H...π(naphthalene){*R**-B} [C21–H21C...Cg = 2.96 Å; Cg = C29–C30–C31–C32–C37–C38 ring]. Molecules of title compound are piled up to form columns along *a*-axis (Figure 3). Each of columns is composed of single conformer of same absolute configuration in crystal packing of title–compound. That is, there are four kinds of columns. In the column composed of conformer (B),

**Table 3.** Interplanar angles and torsion angles of homologues **I**, **II**, and title compound.

| **Angles** | **Homologue I** | **Title compound** | | | | **Homologue II** | |
|---|---|---|---|---|---|---|---|
| | | **Conformer (G)** | | **Conformer (B)** | | | |
| *Interplanar angles* | | | | | | | |
| Ph-Ph | 12.18 | 51.48(9) | | 51.26(9) | | 50.35(7) | |
| Ph(H)-nap | 80.25(6) | 71.15(8) | | 75.61(7) | | | |
| Ph(3,5-diMe)-nap | | | 79.93(7) | | 87.95(7) | 81.87(6) | 83.55(6) |
| *Torsion angles* | | | | | | | |
| car(H)-nap | -76.73(16) | 110.62 | | -105.04 | | | |
| car(3,5-diMe)-nap | | | 117.31 | | -114.43 | 113.52(15) | 102.95(16) |
| car(H)-Ph | 179.76(13) | 169.47 | | -173.49 | | | |
| car(3,5-diMe)-Ph | | | 152.56 | | -145.05 | 153.91(13) | 164.07(13) |

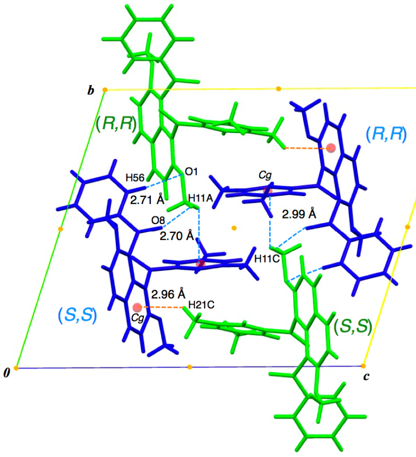

**Figure 2**. Head-to-head fashioned 3,5-dimethylbenzoyl groups of title compound in asymmetric unit.

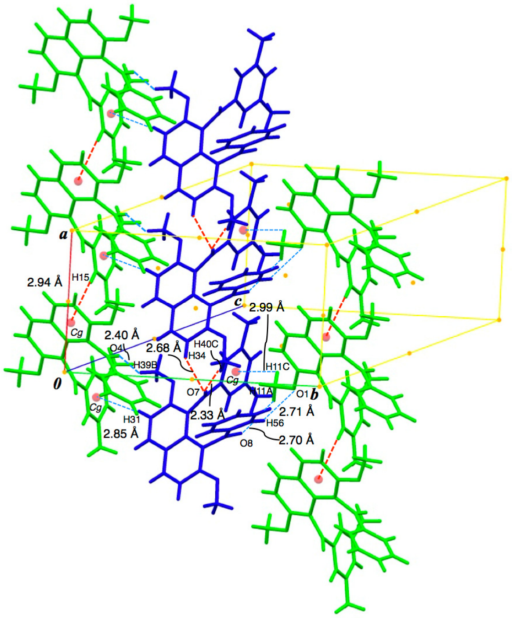

**Figure 3.** Column forming hydrogen bonds between identical enantiomers (red-dashed lines) and intercolumn hydrogen bonds between (*S,S*)-enantiomers for conformer (B) and (*R,R*)-enantiomers for conformer (G) (sky blue-dashed lines).

the molecules are linked by two types of C–H...O=C hydrogen bonds, *i.e.*, (2-methoxy)C–H...O=C(3,5-dimethylbenzoyl) hydrogen bond between the methoxy group at 2-position of the naphthalene ring and the 3,5-dimethylbenzoyl group [C40–H40C...O7 = 2.33 Å] and (naphthalene)C–$\mathrm{H}_{(3\text{-})}$...O=C hydrogen bond [C34–H34...O7 = 2.68 Å] between hydrogen at 3-position of the naphthalene ring and the 3,5-dimethylbenzoyl group. In the column composed of conformer (G) the molecules are connected *via* (3,5-dimethylbenzene)C–H...π(naphthalene) hydrogen bonds between methyl group of 3,5-dimethylbenzene ring and the naphthalene ring [C15–H15...Cg = 2.94 Å; Cg = C5–C10 ring]. The column of *R,R*-isomers of conformer (*R*-B), that of *S,S*-isomers of conformer (*S*-G), that of *S,S*-isomers of conformer (*S*-B), and that of *R,R*-isomers of conformer (*R*-G) are aggregated in rectangular fashion through circularly aligned weak non-classical hydrogen bonds. The rectangular-shaped column aggregates are connected to each other with {*R**-B}(7-methoxy)C–H...O=C(benzoyl){*S**-G} hydrogen bonds between methoxy group at 7-position of the naphthalene ring and benzoyl group [C39–H39B...O4 = 2.40 Å] and {*R**-B}(naphthalene)C–$\mathrm{H}_{(6\text{-})}$...π(3,5-dimethylbenzene){*S**-G} between hydrogen at 6-position of the naphthalene ring and 3,5-dimethyl benzene ring [C31–H31...Cg = 2.85 Å; Cg = C14–C19 ring] along *b*-axis resulting in formation of bilayer structure of molecular aggregates (Figure 4). However, there are no effective hydrogen bonds observed between the exterior sides of the bilayers along *c*-axis.

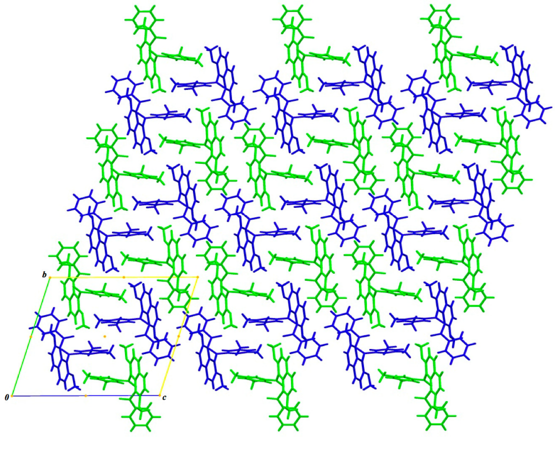

**Figure 4.** Molecular packing structure of title compound viewed down *a*-axis.

Several years ago, the authors reported crystal structures of symmetrical homologues of title compound, 1,8-dibenzoyl-2,7-dimethoxynaphthalene (**I**) [25] and 1,8-bis(3,5-dimethyl benzoyl)-2,7-dimethoxynaphthalene (**II**) [26] (Figure 5). The interplanar angles and the torsion angles of the homologues **I**, **II**, and title compound are summarized in Table 3. Among these compounds, only title compound has conformers. Two different aroyl groups in title compound apparently produce the unique spatial situation reflected by respective symmetrical homologues. The non-substituted benzoyl groups in both

**Table 4.** Non-covalent bonding interactions observed in homologues **I**, **II**, and title compound *.

| | **Homologue I** | **Homologue II** | **Title compound** |
|---|---|---|---|
| *Column forming interactions between identical enantiomers* | | | |
| (2-methoxy)C–H…O=C(3,5-dimethylbenzene) | | | 2.325 |
| (naphthalene)C–$H_{(3-)}$…O=C(3,5-dimethylbenzene) | | 2.554 | |
| (2-methoxy)C–H…O=C(3,5-dimethylbenzene) | | 2.593 | |
| (naphthalene)C–$H_{(3-)}$…O=C(3,5-dimethylbenzene) | | | 2.677 |
| (3,5-dimethylbenzene)C–H…π(naphthalene) | | | 2.94 |
| *Intercolumn between identical enantiomers* | | | |
| (2-methoxy)C–H…O=C(benzoyl) | 2.39 | | |
| (benzene)C–$H_{(3-)}$…O=C(benzoyl) | 2.6 | | |
| {G}(methyl)C–H…π(naphthalene){B} | | | 2.96 |
| *Intercolumn between opposite enantiomers* | | | |
| (7-methoxy)C–H…O=C(3,5-dimethylbenzoyl) | | 2.41 | |
| {B}(7-methoxy)C–H…O=C(benzoyl){G} | | | 2.401 |
| {G}(7-methoxy)C–H…O=C(benzoyl){B} | | | 2.702 |
| {B}(benzoyl)C–$H_{(o-)}$…O(7-methoxy){G} | | | 2.713 |
| {B}(naphthalene)C–$H_{(6-)}$…π(3,5-dimethylbenzene){G} | | | 2.846 |
| {G}(7-methoxy)C–H…π(3,5-dimethylbenzene){B} | | | 2.988 |
| π…π Cg…Cg | 3.6383 | | |
| Interplanar distance | 3.294 | | |

* Non-covalent bonding interactions between common moieties are underlined.

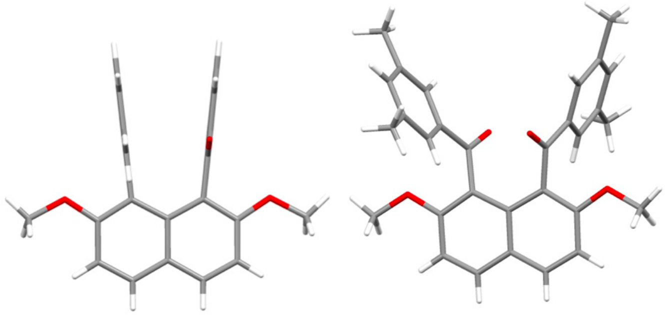

**Figure 5.** Single molecular structures of symmetrical homologues **I** (left) and **II** (right).

conformers of title compound make smaller interplanar angles with the naphthalene ring than homologue **I**, whereas 3,5-dimethylbenzoyl groups in both conformers of title compound forms larger interplanar angles than homologue **II** [71.15° for conformer (G) and 75.61° for conformer (B) vs. 80.25(6)° for homologue **I**; 79.93° for conformer (G) and 87.95° for conformer (B) vs. 81.87(6)° and 83.55(6)° for homologue **II**]. Figures 6 and 7 show molecular packing structures viewed down *b*-axis of homologues **I** and **II**, respectively. In the case of homologue **I**, identical enantiomeric isomers are aligned into face-to-side fashion along *a*-axis, and piled up unidirectionary forming columns along *b*-axis. Accordingly, sheets structure spreading in *ab*-plane is produced. The sheets are alternately stacked into layers with the other sheet composed of counterpart enantiomers along *c*-axis. In the crystal packing of homologue **II**, identical enantiomers are aligned along *a*-axis in head-to-head fashion overlapping the 3,5-dimethylbenzene moieties. The molecules are piled up forming columns along *b*-axis. The sheets spreading in *ab*-plane thus yielded are alternately stacked to make layer structure with the other sheet composed of counter enantiomers along *c*-axis. Title compound and homologue **II** have common spatial organization topology in which 3,5-dimethylbenzene rings are aligned in head-to-head orientation (Figures 2 and 8). Table 4 shows non-covalent bonding interactions observed in crystals of title compound and the two symmetrical homologues. They are classified as three categories, *i.e.*, column forming hydrogen bonds between identical enantiomers, intercolumn hydrogen bonds between identical enantiomers, and intercolumn hydrogen bonds between opposite enantiomers. Title compound has many common features with homologue **II**. Homologue **I** has no effective column forming interactions between identical enantiomers. The molecular packing of homologue **I** is mainly stabilized by two types of intercolumn hydrogen bonds, intercolumn hydrogen bonds between identical enantiomers as (2-methoxy)C–H…O=C(benzoyl) and (benzene)C–$H_{(3-)}$…O=C(benzoyl) hydrogen bonds and those between opposite enantiomers as π…π stacking interactions. On the other hand, homologue **II** and title compound have column-forming interactions between identical enantiomers and intercolumn hydrogen bonds between opposite enantiomers, whereas they have no effective intercolumn hydrogen bonds between identical enantiomers. Furthermore, title compound and homologue **II** form common hydrogen bonding interactions at the corresponding positions to each other, *i.e.*, (2-methoxy)C–H…O=C(3,5-dimethylbenzoyl) hydrogen bonds and (3-position of naphthalene ring)C–H…O=C(3,5-dimethyl benzoyl) for column forming interactions, and (7-methoxy)C–H…O=C(3,5-dimethylbenzoyl or benzoyl) for intercolumn interactions between opposite enantiomers. In the column forming interactions of title compound, one has shorter distance and the other has longer than those of homologue **II** (2.33 Å and 2.68 Å for title compound vs. 2.59 Å and 2.55 Å for homologue **II**). In the intercolumn interactions between opposite enantiomers of title compound, almost same distance interaction and longer one than homologue **II** are observed between conformers (2.40 Å and 2.70 Å vs. 2.41 Å). These data indicate that title compound requires weak interactions with almost the same or stronger hydrogen bonds than homologue **II** (2.33 Å and 2.68 Å; 2.40 Å and 2.70 Å). Furthermore, title compound has a number of weak hydrogen bonds that homologue **II** lacks, including {*R**-G}(3,5-dimethylbenzene)C–H…π(naphthalene){*R**-G} (2.94 Å), {G}(methyl)C–H…π(naphthalene){B} (2.96 Å), {*R**-B}(benzoyl)C–H…OMe(7-methoxy){*S**-G} (2.71 Å), {*R**-B}(naphthalene)C–$H_{(6-)}$…π(3,5-dimethyl benzene){*S**-G} (2.85 Å), and {*R**-G}(7-methoxy)C–H…π(3,5-

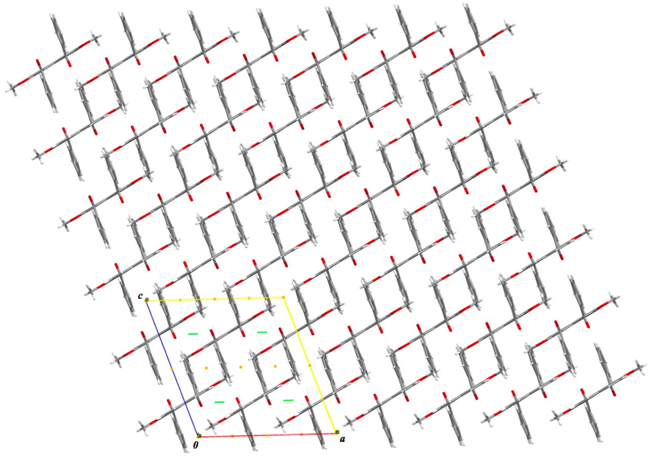

**Figure 6.** Molecular packing structure of homologue **I** viewed down *b*-axis.

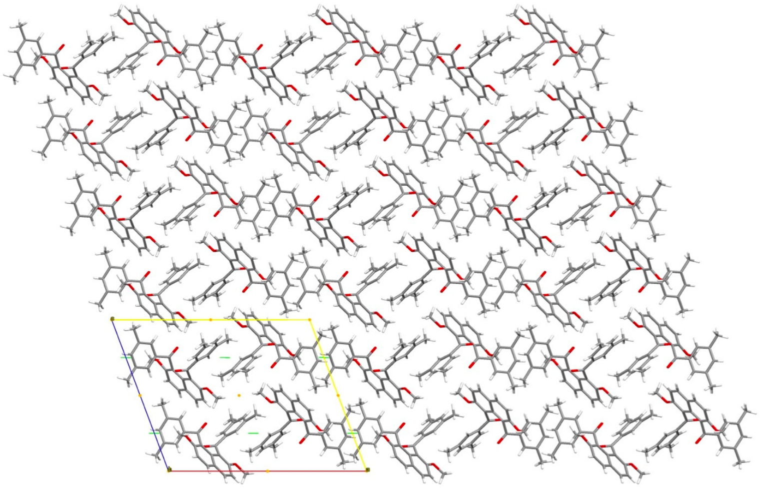

**Figure 7.** Molecular packing structure of homologue **II** viewed down *b*-axis.

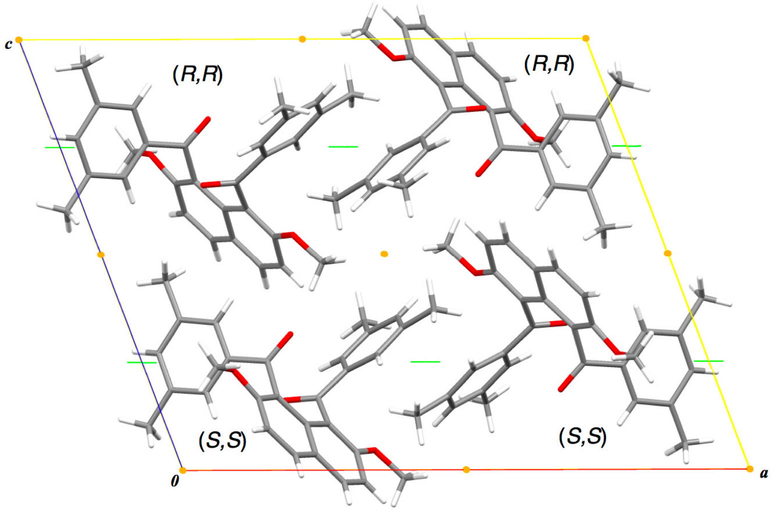

**Figure 8.** Head-to-head fashioned 3,5-dimethylbenzoyl groups of homologue **II** in asymmetric unit.

dimethylbenzene){*S**-B} (2.99 Å). Most of the weak hydrogen bonds are observed between conformer (B) and conformer (G), *i.e.*, {*R**-G}(methyl)C–H…π(naphthalene){*R**-B} (2.96 Å), {*R**-B}(benzoyl)C–H$_{(o\text{-})}$…OMe(7-methoxy){*S**-G} (2.71 Å), {*R**-B}(naphthalene)C–H$_{(6\text{-})}$…π(3,5-dimethylbenzene){*S**-G} (2.85 Å), and {*R**-G}(7-methoxy)C–H…π(3,5-dimethylbenzene){*S**-B} (2.99 Å). Especially, three weak interactions, {*R**-G}(methyl)C–H…π(naphthalene){*R**-B} (2.96 Å), {*R**-B}(benzoyl) C–H…OMe(7-methoxy){*S**-G} (2.71 Å), and {*R**-G}(7-methoxy) C–H…π(3,5-dimethylbenzene){*S**-B} (2.99 Å), are observed in the rectangular-shaped tetrameric conformer aggregate. These data show that crystal packing of title compound is stabilized by accumulation of a number of weak interactions. Among the weak non-covalent interactions, title compound shows two types of C–H…O=C non-classical hydrogen bonds, which is essentially the same situation as for homologue **II**. However, the C–H…O=C hydrogen bonds in title compound bear rather disproportionated balance in comparison to those of homologue **II** (2.33 Å and 2.68 Å for title compound vs. 2.55 Å and 2.59 Å for homologue **II**). This structural feature is plausibly originated from unsymmetrical spatial organization of title compound. To form dense crystal packing, title compound is obliged to adopt two conformers in the asymmetric unit cell. Two conformers cooperatively stabilize the crystal packing by forming many weak hydrogen bonds. Title compound might be to attain the maximum stabilization by formation of the rectangular-shaped tetrameric conformer aggregates with head-to-head oriented alignment of 3,5-dimethylbenzoyl groups as suitable spatial organization for accumulating a number of weak hydrogen bonds.

## 4. Conclusion

Crystal structure of 1-benzoyl-8-(3,5-dimethylbenzoyl)-2,7-dimethoxynaphthalene has been determined and the structural features are systematically compared with the symmetrical homologues, 1,8-dibenzoyl-2,7-dimethoxynaphthalene (**I**) and 2,7-dimethoxy-1,8-bis(3,5-dimethylbenzoyl) naphthalene (**II**). The spatial organization of aroyl groups in the single molecular structure shows essentially the same topology for title compound and two symmetrically substituted homologues. On the other hand, the crystal packing structure of title compound is highly similar to homologue **II**. The crystal packing of homologue **I** is determined dominantly by sole function of strong non-classical hydrogen bonds and π…π stacking. The crystal packing of homologue **II** is stabilized by moderate and weak non-classical hydrogen bonds. If strong non-covalent bonding interactions largely contribute to determine crystal packing, title compound might exhibit topologically same crystal packing for homologue **I**. In other words, spatial organization of 3,5-dimethylbenzoyl groups affords larger influence than benzoyl group in determination of the crystal packing. Consequence of this, accumulation of large number of far weak non-classical hydrogen bonds preferentially contributes largely to stabilization of the crystal packing rather than sole function of strong non-classical hydrogen bonds and π…π stacking.

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## Supplementary material

All crystallographic data for this paper are deposited in Cambridge Crystallographic Data Centre (CCDC1541862). The data can be obtained free of charge at 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.

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