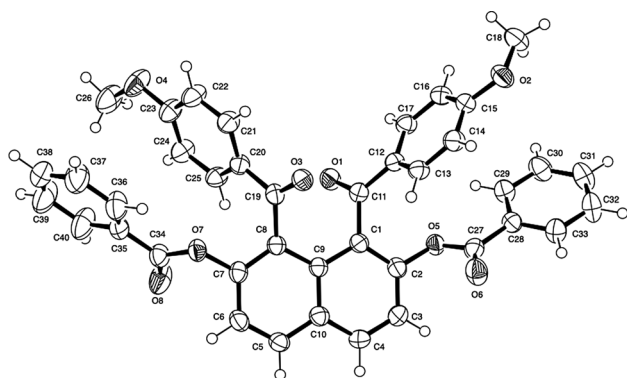


Miyuki Kobayashi, Kikuko Iida, Hiroaki Iitsuka, Kun Li, Noriyuki Yonezawa and Akiko Okamoto\*

# The crystal structure of 1,8-bis(4-methoxybenzoyl)naphthalene-2,7-diyl dibenzoate, C<sub>40</sub>H<sub>28</sub>O<sub>8</sub>



**Table 1:** Data collection and handling.

Crystal:	Colorless block
Size:	0.40 × 0.30 × 0.10 mm
Wavelength:	Cu K $\alpha$ radiation (1.54187 Å)
$\mu$ :	0.78 mm <sup>-1</sup>
Diffractometer, scan mode:	Rigaku R-Axis RAPID, $\omega$
$\theta_{\max}$ , completeness:	68.2°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	44,449, 5717, 0.032
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 5474
$N(\text{param})_{\text{refined}}$ :	436
Programs:	Rigaku [1, 2], SIR2004 [3], SHELX [4], ORTEP-III [5], PLATON [6]

<https://doi.org/10.1515/ncrs-2021-0160>

Received April 27, 2021; accepted May 17, 2021;

published online June 23, 2021

## Abstract

C<sub>40</sub>H<sub>28</sub>O<sub>8</sub>, orthorhombic,  $Pna2_1$  (no. 33),  $a = 27.0291(4)$  Å,  $b = 14.5593(2)$  Å,  $c = 7.95172(10)$  Å,  $V = 3129.20(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{\text{gt}}(F) = 0.0276$ ,  $wR_{\text{ref}}(F^2) = 0.0690$ ,  $T = 193$  K.

CCDC no.: 2084108

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

## Source of material

The title compound was prepared by reaction of 1,8-bis(4-methoxybenzoyl)-2,7-dihydroxynaphthalene (0.2 mmol,

85.7 mg), which was obtained *via* P<sub>2</sub>O<sub>5</sub>-MsOH [7]-mediated diarylation of 2,7-dihydroxynaphthalene and 4-methoxybenzoic acid, benzoyl chloride (0.44 mmol, 61.9 mg), and triethylamine (0.22 mmol, 0.03 ml) in dichloromethane (0.5 ml). After the reaction mixture was stirred at room temperature for 3 h, it was poured into water (30 ml) and the mixture was extracted with CHCl<sub>3</sub> (10 ml × 3). The combined extracts were washed with sat. NaHCO<sub>3</sub> aq. and brine. The organic layers thus obtained were dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure to give the crude product (94%). <sup>1</sup>H NMR  $\delta$  (400 MHz, CDCl<sub>3</sub>): 3.73 (6H, s), 6.72 (4H, broad), 7.25 (4H, t,  $J = 6.4$  Hz), 7.46 (2H, t,  $J = 6.0$  Hz), 7.56 (2H, d,  $J = 7.6$  Hz), 7.63 (4H, d,  $J = 6.0$  Hz), 7.69 (4H, broad), 8.10 (2H, d,  $J = 7.6$  Hz) ppm. <sup>13</sup>C NMR  $\delta$  (75 MHz, CDCl<sub>3</sub>): 55.45, 113.52 (overlap), 122.11, 128.31, 128.48, 129.68, 129.99, 130.82, 131.38, 131.54, 133.61, 147.54, 163.64, 164.18, 193.36 ppm. IR (KBr): 3450 (C–H), 2838 (O–CH<sub>3</sub>), 1735 (OC=O), 1653 (C=O), 1599 (Ar), 1507 (Ar) cm<sup>-1</sup>. HRMS ( $m/z$ ):  $[M+H]^+$  calcd. for C<sub>40</sub>H<sub>29</sub>O<sub>8</sub>, 637.1863, found, 637.1910. **m.p.** = 184.6–185.0 °C.

\*Corresponding author: Akiko Okamoto, Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei, Tokyo, Japan, E-mail: aokamoto@cc.tuat.ac.jp. <https://orcid.org/0000-0002-4148-0798>

Miyuki Kobayashi, Kikuko Iida, Hiroaki Iitsuka, Kun Li and Noriyuki Yonezawa, Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei, Tokyo, Japan

## Experimental details

All H atoms were found in a difference map and were subsequently refined as riding atoms, with C–H = 0.95 (aromatic) and 0.98 (methyl) Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
O1	0.29041 (5)	0.41345 (10)	0.86408 (19)	0.0422 (3)
O2	0.13130 (6)	0.13796 (11)	1.1669 (2)	0.0505 (4)
O3	0.26450 (5)	0.28654 (9)	0.5490 (2)	0.0403 (3)
O4	0.49626 (6)	0.24230 (11)	0.6109 (3)	0.0622 (5)
O5	0.16377 (5)	0.50203 (10)	0.92579 (17)	0.0367 (3)
O6	0.09082 (6)	0.46659 (13)	0.8054 (2)	0.0544 (4)
O7	0.33903 (5)	0.41496 (9)	0.24556 (18)	0.0368 (3)
O8	0.39186 (6)	0.53448 (11)	0.2487 (3)	0.0653 (5)
C1	0.22243 (7)	0.46811 (13)	0.7096 (2)	0.0323 (4)
C2	0.18339 (7)	0.52016 (14)	0.7655 (3)	0.0363 (4)
C3	0.16461 (8)	0.59593 (15)	0.6767 (3)	0.0420 (5)
H3	0.137524	0.630192	0.719852	0.050*
C4	0.18584 (8)	0.61926 (14)	0.5282 (3)	0.0407 (5)
H4	0.173861	0.671224	0.468495	0.049*
C5	0.24628 (7)	0.59382 (14)	0.3044 (3)	0.0384 (5)
H5	0.233473	0.645536	0.245988	0.046*
C6	0.28432 (7)	0.54571 (14)	0.2374 (3)	0.0389 (5)
H6	0.298509	0.563885	0.133266	0.047*
C7	0.30253 (7)	0.46888 (13)	0.3232 (3)	0.0344 (4)
C8	0.28322 (7)	0.43827 (13)	0.4732 (3)	0.0319 (4)
C9	0.24404 (7)	0.49011 (12)	0.5495 (2)	0.0314 (4)
C10	0.22535 (7)	0.56790 (14)	0.4607 (3)	0.0350 (4)
C11	0.24682 (7)	0.40204 (13)	0.8329 (3)	0.0331 (4)
C12	0.21717 (7)	0.33013 (13)	0.9162 (2)	0.0332 (4)
C13	0.23196 (7)	0.29951 (13)	1.0742 (3)	0.0372 (4)
H13	0.261607	0.322872	1.122056	0.045*
C14	0.20447 (7)	0.23586 (15)	1.1630 (3)	0.0401 (5)
H14	0.214743	0.216418	1.271590	0.048*
C15	0.16175 (7)	0.20081 (13)	1.0915 (3)	0.0383 (5)
C16	0.14703 (8)	0.22875 (14)	0.9315 (3)	0.0392 (5)
H16	0.118268	0.203033	0.881516	0.047*
C17	0.17416 (7)	0.29355 (14)	0.8461 (3)	0.0360 (4)
H17	0.163532	0.313603	0.738288	0.043*
C18	0.14346 (10)	0.10974 (18)	1.3333 (3)	0.0570 (6)
H18A	0.145922	0.163815	1.406193	0.068*
H18B	0.175225	0.077275	1.332191	0.068*
H18C	0.117622	0.068685	1.375994	0.068*
C19	0.29736 (7)	0.34343 (13)	0.5353 (2)	0.0337 (4)
C20	0.34972 (7)	0.32091 (13)	0.5668 (3)	0.0356 (4)
C21	0.36423 (8)	0.22857 (14)	0.5707 (3)	0.0422 (5)
H21	0.339964	0.181619	0.561617	0.051*
C22	0.41302 (8)	0.20543 (15)	0.5874 (4)	0.0496 (6)
H22	0.422356	0.142538	0.589969	0.060*
C23	0.44902 (8)	0.27307 (16)	0.6007 (3)	0.0470 (5)
C24	0.43507 (8)	0.36500 (15)	0.6039 (3)	0.0462 (5)
H24	0.459316	0.411667	0.617341	0.055*
C25	0.38586 (7)	0.38792 (14)	0.5873 (3)	0.0399 (5)
H25	0.376431	0.450767	0.589881	0.048*
C26	0.53508 (9)	0.3078 (2)	0.6011 (5)	0.0716 (8)
H26A	0.533231	0.349302	0.697866	0.086*
H26B	0.531783	0.343284	0.496972	0.086*
H26C	0.567026	0.275940	0.601610	0.086*
C27	0.11558 (8)	0.47378 (14)	0.9297 (3)	0.0387 (5)
C28	0.09848 (8)	0.45404 (13)	1.1030 (3)	0.0362 (4)
C29	0.13081 (8)	0.44668 (16)	1.2368 (3)	0.0442 (5)

## Comment

Weak interactions in solid organic molecular substances have acquired growing interests and the consequent reevaluation over the last two decades [8–10]. Since the degree of freedom in arranging aromatic rings is small, crystals of compounds of non-coplanarly accumulated aromatic rings can be expected to distinguish contributions of rather weak non-covalent bonding interactions other than  $\pi \cdots \pi$  stacking interactions or classical hydrogen bonds as structure determining factors [11–13].

In the molecular structure of the title compound, the benzene rings of 1,8-(4-methoxybenzoyl) groups and those of 2,7-benzoyloxy groups are twisted away from the naphthalene ring (Figure). Two 1,8-(4-methoxybenzoyl) groups are situated in anti-orientation. The dihedral angles between the benzene rings of 4-methoxybenzoyl groups and the naphthalene ring system are 67.41(7)° [C20–C25 ring, C7–C8–C19–O3 torsion angle = –116.81(15)°] and 73.77 (6)° [C12–C17 ring C2–C1–C11–O1 torsion angle = –119.46(15)°], respectively. The dihedral angle between the best planes of the two phenyl rings is 63.18(8)°. The two benzoyloxy groups at 2,7-positions of the naphthalene moiety are also situated in opposite directions. The dihedral angles between their benzene rings [C35–C40 ring and C28–C33 ring] and the naphthalene ring system are 72.13(9)° and 53.08(7)°, respectively. The two benzene rings make a dihedral angle of 77.55(10)°. The phenyl rings and carbonyloxy moieties are almost coplanar [O8–C34–C35–C36 torsion angle = –171.15(19)° and O6–C27–C28–C29 torsion angle = 167.41(16)°]. Several non-classical hydrogen bonds exhibiting almost similar interatomic distances are also confirmed: C–H(methoxy)⋯O=C(benzoyl) (2.57 Å, H18B⋯O1; 1/2–*x*, –1/2+*y*, 1/2+*z*), C–H(naphthalene)⋯O=C(benzoyl) (2.58 Å, H5⋯O3; 1/2–*x*, –1/2+*y*, 1/2+*z*), C–H(benzoyloxy)⋯OMe (2.60 Å, H39⋯O2; 1/2+*x*, 1/2–*y*, –1+*z*), and and C–H(benzoyloxy)⋯O(benzoyloxy) (2.60 Å, H31⋯O6; *x*, *y*, 1+*z*). The first three non-classical hydrogen bonds are parallel to the glide planes, and the last one is oriented along the *c* axis. The authors reported the crystal structure of the homologous compounds [2,7-dimethoxy-8-(4-methoxybenzoyl)-naphthalen-1-yl]([4-methoxyphenyl)methanone chloroform monosolvate (I) [14] and 1,8-dibenzoylnaphthalene-2,7-diyl dibenzoate (II) [15]. The title compound and the homologue II shows unsymmetric spatial situation of 1,8-diaroyl groups on naphthalene ring [dihedral angles between phenyl rings and naphthalene: 67.41(7)° and 73.77(6)° for the title compound, 67.12(5)° and 85.15(5)° for homologue II, and 72.51(7)° and 73.33(7)° for homologue I].

Table 2: (continued)

Atom	x	y	z	U <sub>iso</sub> */U <sub>eq</sub>
H29	0.165393	0.453749	1.219787	0.053*
C30	0.11237 (10)	0.42890 (18)	1.3959 (3)	0.0527 (6)
H30	0.134439	0.423525	1.488397	0.063*
C31	0.06230 (10)	0.41897 (18)	1.4210 (3)	0.0564 (6)
H31	0.049884	0.407391	1.530749	0.068*
C32	0.03018 (9)	0.4258 (2)	1.2874 (3)	0.0565 (6)
H32	-0.004362	0.418441	1.304900	0.068*
C33	0.04805 (8)	0.44328 (16)	1.1281 (3)	0.0455 (5)
H33	0.025869	0.447931	1.035841	0.055*
C34	0.38375 (8)	0.45543 (15)	0.2158 (3)	0.0423 (5)
C35	0.42021 (8)	0.39016 (15)	0.1459 (3)	0.0431 (5)
C36	0.40780 (9)	0.30444 (16)	0.0899 (4)	0.0560 (6)
H36	0.374231	0.285137	0.091985	0.067*
C37	0.44404 (11)	0.24566 (19)	0.0301 (4)	0.0706 (8)
H37	0.435204	0.186238	-0.009013	0.085*
C38	0.49228 (11)	0.2726 (2)	0.0272 (4)	0.0666 (8)
H38	0.516992	0.231959	-0.013693	0.080*
C39	0.50526 (10)	0.3585 (2)	0.0833 (5)	0.0781 (9)
H39	0.538913	0.377240	0.081522	0.094*
C40	0.46926 (9)	0.4174 (2)	0.1423 (5)	0.0709 (9)
H40	0.478170	0.476900	0.180721	0.085*

Two benzoyloxy groups in homologue II are twisted to the naphthalene ring with almost same dihedral angles [71.47(5)° and 76.41(5)° vs. 72.13(9)° and 53.08(7)° for the title compound]. In these compounds, fewer non-classical hydrogen bonds than in the packing of the title compound are observed, e.g. C–H(naphthalene)⋯OMe for homologue I, C–H(benzoyl)⋯O=C(benzoyl) and C–H(benzoyloxy)⋯π(naphthalene) for homologue II. More effective factors stabilize their crystals such as co-crystallization with solvent molecules or π⋯π stacking interactions. In other words, continuous neighbouring substitution of 4-methoxybenzoyl groups and benzoyloxy group disturb the effective interactions other than non-classical hydrogen bonds in title compound. Concludingly, neighbourly aligned four benzene rings on naphthalene ring afford enough stabilization with the aid of maximum number of non-classical hydrogen bonds in the absence of π⋯π stacking. The magnitude of the stabilization satisfactorily compensates those expected by intermolecular interaction of crystal solvent.

**Acknowledgement:** The authors express their gratitude to Professor Keiichi Noguchi, Instrumentation Analysis Center, Tokyo University of Agriculture and Technology, for technical advice.

**Author contributions:** All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

**Research funding:** JSPS KAKENHI Grant Number JP20K05473. Tokyo Ohka Foundation for The Promotion of Science and Technology Grant Number 216065.

**Conflict of interest statement:** The authors declare no conflicts of interest regarding this article.

## References

1. Rigaku. PROCESS-AUTO; Rigaku Corporation: Tokyo, Japan, 1998.
2. Rigaku. CRYSTALSTRUCTURE; Rigaku Corporation: Tokyo, Japan, 2010.
3. Burla M. C., Caliandro R., Camalli M., Carrozzini B., Cascarano G. L., De Caro L., Giacovazzo C., Polidori G., Spagna R. SIR2004: an improved tool for crystal structure determination and refinement. *J. Appl. Crystallogr.* 2005, *38*, 381–388.
4. Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
5. Burnett M. N., Johnson C. K. ORTEPIII. Report ORNL-6895; Oak Ridge National Laboratory: Tennessee, USA, 1996.
6. Spek A. L. Structure validation in chemical crystallography. *Acta Crystallogr.* 2009, *D65*, 148–155.
7. Eaton P., Carlson G. R., Lee J. T. Phosphorus pentoxide-methane sulfonic acid. convenient alternative to polyphosphoric acid. *J. Org. Chem.* 1973, *38*, 4071–4073.
8. Desiraju G. R., Steiner T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999.
9. Desiraju G. R. C–H⋯O and other weak hydrogen bonds. from crystal engineering to virtual screening. *Chem. Commun.* 2005, *24*, 2995–3001.
10. Taylor R., Kennard O. Crystallographic evidence for the existence of C–H⋯O, C–H⋯N, and C–H⋯Cl hydrogen bonds. *J. Am. Chem. Soc.* 1982, *104*, 5063–5070.
11. Okamoto A., Yonezawa N. Unique and specific reaction behavior and characteristic spatial organization of non-coplanar aromatic-ring-accumulated molecular compounds. *J. Synth. Org. Chem.* 2015, *73*, 339–360.
12. Muto T., Iida K., Noguchi K., Yonezawa N., Okamoto A. Crystal structure and Hirshfeld surface analysis of 2-hydroxy-7-methoxy-1,8-bis(2,4,6-trichlorobenzoyl)naphthalene. *Acta Crystallogr.* 2019, *E75*, 1418–1422.
13. Iitsuka H., Li K., Kobayashi M., Iida K., Yonezawa N., Okamoto A. Crystal structure of 1,2-bis(4-fluorophenyl)-1-hydroxy-2,3,8-trimethoxyacenaphthene: formation of a five-membered intramolecular O–H⋯O hydrogen-bonded ring. *Acta Crystallogr.* 2021, *E77*, 175–179.
14. Sasagawa K., Sakamoto R., Kusakabe T., Okamoto A., Yonezawa N. [2,7-Dimethoxy-8-(4-methoxybenzoyl)naphthalen-1-yl](4-methoxyphenyl)methanone chloroform monosolvate. *Acta Crystallogr.* 2013, *E69*, o146.
15. Sakamoto R., Sasagawa K., Hijikata D., Okamoto A., Yonezawa N. 1,8-Dibenzoylnaphthalene-2,7-diyl dibenzoate. *Acta Crystallogr.* 2012, *E68*, o2454.