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The crystal structure of 1,8-bis(4-methoxybenzoyl)naphthalene-2,7-diyl dibenzoate, $C_{40}H_{28}O_8$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.40 × 0.30 × 0.10 mm
Wavelength:	Cu K α radiation (1.54187 Å)
μ :	0.78 mm ⁻¹
Diffractometer, scan mode:	Rigaku R-Axis RAPID, ω
$\theta_{\max}$, completeness:	68.2°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	44,449, 5717, 0.032
Criterion for I_{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]

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Abstract

$C_{40}H_{28}O_8$, orthorhombic, $Pna2_1$ (no. 33), $a = 27.0291(4)$ Å, $b = 14.5593(2)$ Å, $c = 7.95172(10)$ Å, $V = 3129.20(7)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0276$, $wR_{\text{ref}}(F^2) = 0.0690$, $T = 193$ 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_2O_5 -MsOH [7]-mediated diaroylation 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 $CHCl_3$ (10 ml × 3). The combined extracts were washed with sat. $NaHCO_3$ aq. and brine. The organic layers thus obtained were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give the crude product (94%). ¹H NMR δ (400 MHz, $CDCl_3$): 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. ¹³C NMR δ (75 MHz, $CDCl_3$): 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–CH₃), 1735 (OC=O), 1653 (C=O), 1599 (Ar), 1507 (Ar) cm⁻¹. HRMS (m/z): $[M+H]^+$ calcd. for $C_{40}H_{29}O_8$, 637.1863, found, 637.1910. **m.p.** = 184.6–185.0 °C.

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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 $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
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 revaluation 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) $\cdots$ O=C(benzoyl) (2.57 Å, H18B $\cdots$ O1; 1/2–*x*, –1/2+*y*, 1/2+*z*), C–H(naphthalene) $\cdots$ O=C(benzoyl) (2.58 Å, H5 $\cdots$ O3; 1/2–*x*, –1/2+*y*, 1/2+*z*), C–H(benzoyloxy) $\cdots$ OMe (2.60 Å, H39 $\cdots$ O2; 1/2+*x*, 1/2–*y*, –1+*z*), and and C–H(benzoyloxy) $\cdots$ O(benzoyloxy) (2.60 Å, H31 $\cdots$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
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 $\pi\cdots\pi$ 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 $\pi\cdots\pi$ stacking. The magnitude of the stabilization satisfactorily compensates those expected by intermolecular interaction of crystal solvent.

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