

Crystal structure and Hirshfeld surface analysis of (2,7-diethoxynaphthalene-1,8-diyl)bis[(4-bromophenyl)methanone]

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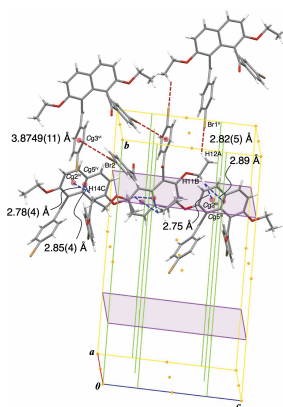
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The title compound, $C_{28}H_{22}Br_2O_4$, crystallizes in the monoclinic space group $P2_1/c$ at 193 K. The two 4-bromobenzoyl groups are attached in a non-coplanar fashion to the naphthalene ring system and are oriented in opposite directions. The two 4-bromobenzene rings are tilted almost symmetrically with respect to the naphthalene ring system. The crystal packing features several kinds of non-classical hydrogen bonds such as $C-H\cdots X$ (X = polar atom), in which the $C-H$ group acts as a hydrogen-atom donor, and $C-H\cdots\pi$ interactions. The two-dimensional fingerprint plots generated in a Hirshfeld surface analysis show non-classical hydrogen bonding with short contacts involving the bromo group.

1. Chemical context

Supramolecular architectures along with supramolecular chemistry have become of interest in recent years from the viewpoint of green chemistry and novel phases of functional device material development (Desiraju, 1989; Lehn, 1995; Atwood *et al.*, 1996; Desiraju *et al.*, 2011). Various building blocks bearing unique functions might be tailored to a supramolecular structure exhibiting desired chemical and physical properties without formation of covalent bonds. The research primarily relies on knowledge of the characteristics of non-covalent bonding interactions, including atomic, geometrical and molecular orientation features (Jeffrey & Saenger, 1991; Steiner & Desiraju, 1998). Attempts to form robust hydrogen bonds involving $CONR_2$ and OH groups, and COOH and NH_2 groups were undertaken both experimentally and theoretically. These have been successfully employed for the preparation of numerous molecular assemblies (Price, 2004; Tanabe *et al.*, 2013; Hubbard *et al.*, 2016). On the other hand, attempts to grasp the nature of weak hydrogen bonds, including non-classical hydrogen bonds where the $C-H$ group acts as a hydrogen-atom donor, for example, have scarcely been achieved, probably because they are often hidden by strong hydrogen bonds. Congested molecules of accumulated aromatic rings have unique spatial structural restrictions such that the aromatic rings are compelled to be arranged in a non-coplanar manner. This structural constraint suggests that the contribution of a parallel overlap of aromatic rings, *i.e.*, $\pi-\pi$ stacking is extremely small. From this viewpoint, the crystal structures of compounds with non-coplanarly accumulated aromatic rings can be expected to emphasize the contributions of rather weak, non-covalent bonding interactions other than $\pi-\pi$ stacking interactions and classical hydrogen bonds. The authors have studied compounds with non-coplanarly accumulated aromatic ring structures in

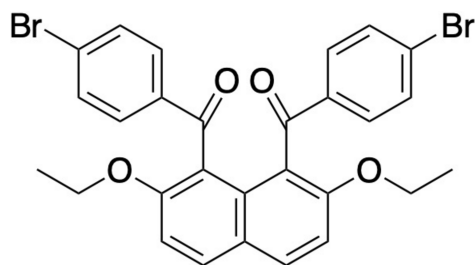


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formation reactions and spatial structures (Okamoto & Yonezawa, 2009, 2015; Okamoto *et al.*, 2011).

peri-Aroylnaphthalene compounds and their homologues usually show an excellent tendency to give single crystallinity, and the crystal structures of over 100 homologues and related compounds have been determined by the authors. With the aid of a systematical comparison of the single molecular structure and accumulation fashion of the crystal structure of series of homologous compounds, the transition of the interaction feature among the homologues has been clarified, which suggests important roles for weak interactions involving C—H hydrogen atoms in the determination of the crystalline spatial placement of molecules (Iida *et al.*, 2022; Kobayashi *et al.*, 2023). Herein, the authors report on the crystal structure and Hirshfeld surface analysis of the title *peri*-aroylnaphthalene, (2,7-diethoxynaphthalene-1,8-diyl)bis[(4-bromophenyl)methanone].



2. Structural commentary

The molecular structure of the title molecule is displayed in Fig. 1. The two 4-bromobenzoyl groups are twisted with respect to the naphthalene ring system and oriented in opposite direction (*anti* orientation). The two 4-bromobenzene rings are tilted almost symmetrically to the naphthalene ring system. The two interplanar angles between the best planes of the 4-bromobenzene rings and the naphthalene ring system are 79.38 (10)° and 79.50 (10)°, respectively

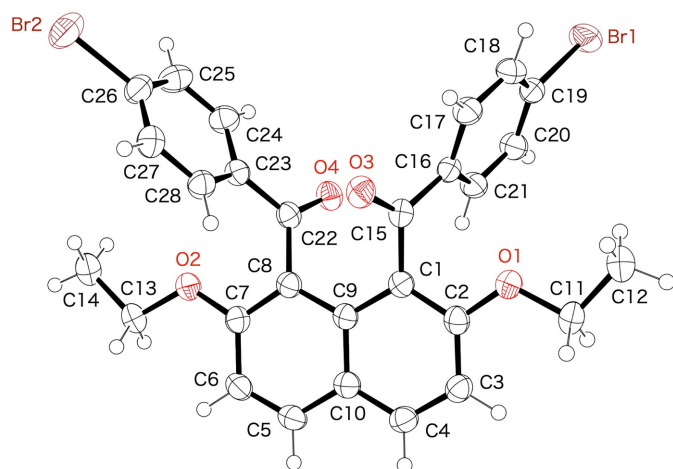


Figure 1

Molecular structure of the title compound with displacement ellipsoids at the 50% probability level.

Table 1

Hydrogen-bond geometry (Å, °).

Cg2, Cg3 and Cg5 are the centroids of the C5–C10, C16–C21 and C1–C10 rings, respectively.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C20—H20...O3 ⁱ	0.95	2.41	3.339 (3)	167
C27—H27...O4 ⁱⁱ	0.95	2.50	3.439 (3)	170
C11—H11B...Cg2 ⁱⁱⁱ	0.99	2.75	3.632 (3)	148
C11—H13B...Cg5 ⁱⁱⁱ	0.99	2.89	3.838 (3)	162
C14—H14C...Cg2 ^{iv}	0.98	2.78 (4)	3.631 (3)	151 (3)
C14—H14C...Cg5 ^{iv}	0.98	2.85 (4)	3.632 (3)	141 (3)
C12—H12A...Br1 ^v	0.97 (4)	2.82 (5)	3.634 (4)	141 (3)
C26—Br2...Cg3 ^{vi}	1.90 (1)	3.88 (1)	5.626 (3)	152 (1)

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$; (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (v) $-x + 2, -y + 2, -z + 1$; (vi) $-x, -y + 2, -z$.

[torsion angles: C9—C1—C15—O3 = 54.9 (3)° and C9—C8—C22—O4 = 50.5 (3)°]. On the other hand, the 4-bromobenzene rings are coplanar with the carbonyl moieties [torsion angles: O3—C15—C16—C21 = −155.7 (2)° and O4—C22—C23—C28 = −155.5 (2)°]. The interplanar angle between the best planes of the two 4-bromobenzene rings is 60.44 (12)°.

3. Supramolecular features

In the crystal, several kinds of non-classical hydrogen bonds ensure the cohesion of the packing. C—H...O=C non-classical hydrogen bonds between the 4-bromobenzene ring and

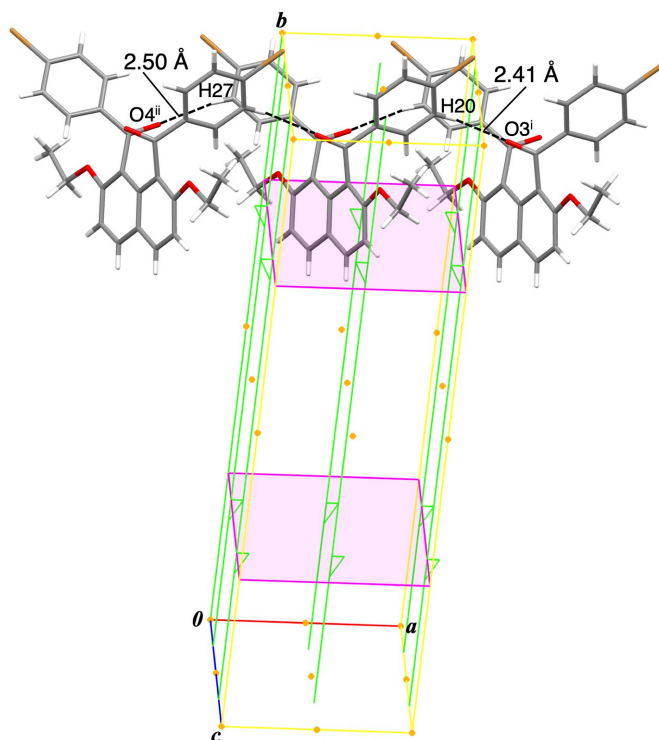


Figure 2

Molecular packing structure of the title compound showing the non-covalent bonding interactions and the relationship with the symmetry elements: C—H...O non-classical hydrogen bonds connect the molecules in a translational relationship along *a*-axis [symmetry codes: (i) $1 + x, y, z$; (ii) $-1 + x, y, z$].

the carbonyl O atom arrange the molecules in a translational relationship along *a*-axis direction [C20—H20···O3ⁱ = 2.41 Å, C27—H27···O4ⁱⁱ = 2.50 Å; symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) −1 + *x*, *y*, *z*] (Table 1, Fig. 2). C—H··· π non-classical hydrogen bonds between the ethoxy moiety and the naphthalene ring system connect the molecules along *ac*-glide plane [C11—H11B···Cg2ⁱⁱⁱ = 2.75 Å, C11—H11B···Cg5ⁱⁱⁱ = 2.89 Å, C14—H14C···Cg2^{iv} = 2.78 (4) Å, C14—H14C···Cg5^{iv} = 2.85 (4) Å; symmetry codes: (iii) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (iv) $x, \frac{3}{2} - y, -\frac{1}{2} + z$; Cg2 and Cg5 are the centroids of the C5–C10 ring and the C1–C10 ring system, respectively] (Fig. 3). The naphthalene ring system acts as hydrogen-atom acceptor of dual Csp³—H··· π non-classical hydrogen bonds. Interactions involving the bromo group are formed complementarily between two molecules, forming centrosymmetric dimeric aggregations [C12—H12A···Br1^v = 2.82 (5) Å, C26—Br2···Cg3^{vi} = 3.8749 (11) Å; symmetry codes: (v) 2 − *x*, 2 − *y*, 1 − *z*; (vi) −*x*, 2 − *y*, −*z*; Cg3 is the centroid of the C16–C21 ring] (Fig. 3).

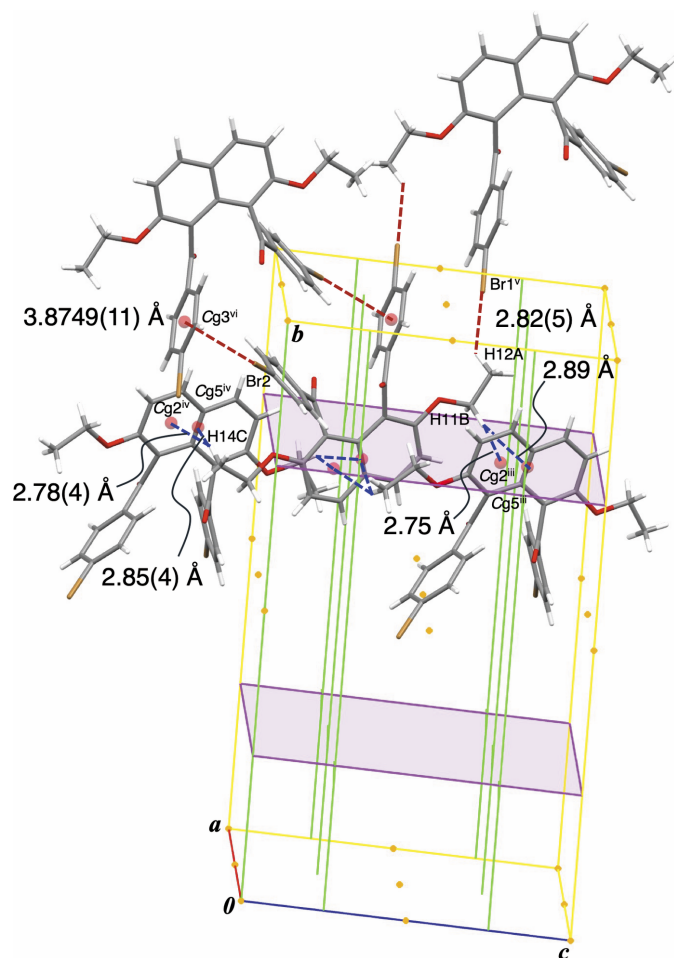


Figure 3

Crystal packing structure of title compound showing non-covalent bonding interactions and the relationship with symmetry elements. C—H··· π non-classical hydrogen bonds connect the molecules along the *ac*-glide plane [symmetry codes: (iii) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (iv) $x, \frac{3}{2} - y, -\frac{1}{2} + z$]. C—H···Br non-classical hydrogen bonds and C—Br··· π short contacts link pairs of molecules centrosymmetrically along the *b*-axis [symmetry codes: (v) 2 − *x*, 2 − *y*, 1 − *z*; (vi) −*x*, 2 − *y*, −*z*].

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.45, update of November 2023; Groom *et al.*, 2016) for the 1,8-dibenzoylnaphthalene and 1,8-diaroyl-2,7-dialkoxynaphthalene frameworks of the title compound yields 39 and 29 hits, respectively. The structure of the title compound exhibits non-coplanarly accumulated aromatic rings, as found in the bromo group-free 1,8-dibenzoylnaphthalene homologues, the bromo group-bearing 1,8-dibenzoylnaphthalene, and 1-benzoylnaphthalene homologues, *viz.* 1,8-dibenzoyl-2,7-dimethoxynaphthalene (CSD refcode XIYSEE; Nakaema *et al.*, 2008), 1,8-dibenzoyl-2,7-diethoxynaphthalene (CSD refcode NEQRUY; Isogai *et al.*, 2013), 1,8-bis(4-bromobenzoyl)-2,7-dimethoxynaphthalene (CSD refcode DUNRUA; Watanabe *et al.*, 2010), (8-[4-(bromomethyl)benzoyl]-2,7-dimethoxynaphthalen-1-yl)[4-(bromomethyl)phenyl]methanone (CSD refcode EVIWUC; Sasagawa *et al.*, 2011), (2,7-dimethoxynaphthalen-1-yl)(phenyl)methanone (CSD refcode KABGAX; Kato, Nagasawa, Hijikata *et al.*, 2010), and 2,7-dimethoxy-1-(4-bromobenzoyl)naphthalene (CSD refcode VACLIW; Kato, Nagasawa, Tsumuki *et al.*, 2010). The dihedral angle between the benzene ring and the naphthalene ring system in 1,8-dibenzoyl-2,7-dimethoxynaphthalene (XIYSEE) is larger than in the 2,7-diethoxy homologues (NEQRUY), *i.e.*, 83.59 (5)° vs 68.42 (5) and 71.69 (5)°. On the other hand, the 4-bromobenzoyl group-bearing homologues exhibit the opposite tendency, *viz.* 70.18 (11) and 74.98 (12)° for 1,8-bis(4-bromobenzoyl)-2,7-dimethoxynaphthalene (DUNRUA) vs 79.38 (10) and 79.50 (10)° for the title compound. The homologue bearing a bromo group bonded to an *sp*³ carbon atom (EVIWUC) has almost the same dihedral angles as the 2,7-dimethoxynaphthalene homologue (DUNRUA) [70.98 (13) and 72.89 (13)°]. The 1-benzoylated homologue (KABGAX) affords three conformers, which have different dihedral angles between the benzene ring and the naphthalene ring system [75.34 (7), 86.47 (7) and 76.55 (6)°]. The homologue with a bromo group gives solely one type of conformer, even if it is 1-monoaroylated homologue [VACLIW; 72.02 (9)°]. Therefore, the introduction of a bromo group at the benzoyl groups at the 1,8-positions has a larger effect on the dihedral angle than an ethoxy group at the 2,7-positions. Furthermore, intra/intermolecular interactions involving the bromo groups contribute significantly to the three-dimensional molecular structure and packing structure.

5. Hirshfeld surface analysis and two-dimensional fingerprint plots

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) was performed and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were generated with *Crystal-Explorer17* (Turner *et al.*, 2017). The Hirshfeld surfaces are colour-mapped with the normalized contact distance, *d*_{norm}, from red (distances shorter than the sum of the van der Waals radii) through white to blue (distances longer than the sum of the van der Waals radii). The Hirshfeld surface of the title

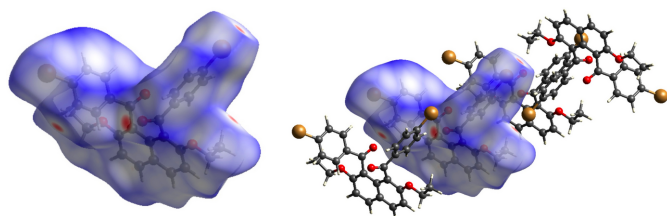


Figure 4

The Hirshfeld surface of the title compound mapped over d_{norm} (left). Several large red points are assigned as O3...H20, O5...H27, and Br1...H12A short contacts (right).

compound mapped over d_{norm} in the range -0.2470 to 1.3548 a.u. is shown in Fig. 4 (left). The red points represent close contacts and negative d_{norm} values on the surface. Several large red points correspond to the short contacts involving the carbonyl O atoms, O3ⁱ and O4ⁱⁱ, and hydrogen atoms, H20 and H27 [symmetry codes: (i) $1 + x, y, z$; (ii) $-1 + x, y, z$], and short Br1^v...H12A interactions [symmetry code: (v) $2 - x, 2 - y, 1 - z$] (Fig. 4, right).

The two-dimensional fingerprint plots from the Hirshfeld surface analysis are shown in Fig. 5, revealing the intermolecular contacts and their percentage contributions to the

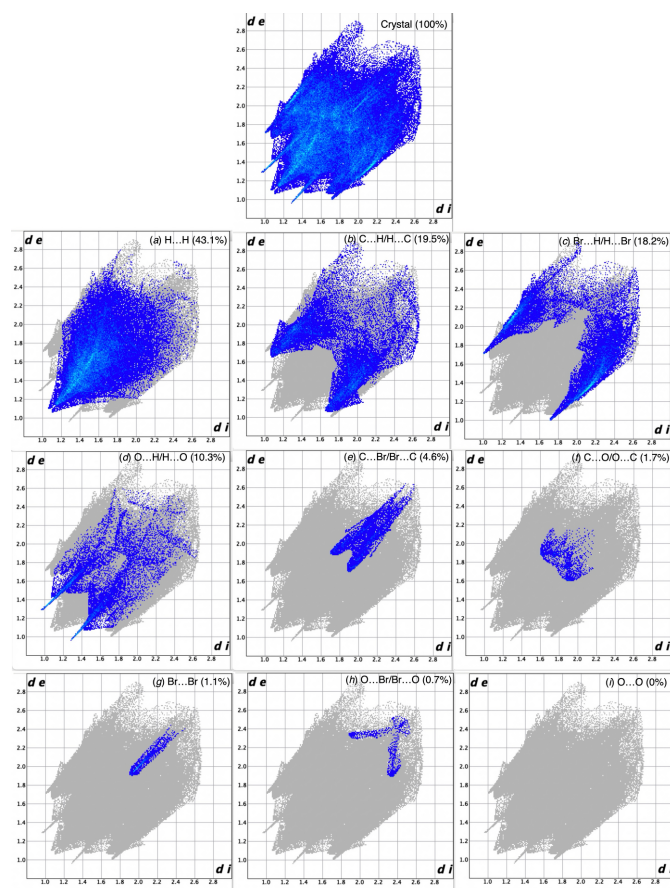


Figure 5

The full two-dimensional fingerprint plot for the title compound, and those delineated into (a) H...H, (b) C...H/H...C, (c) Br...H/H...Br, (d) O...H/H...O, (e) C...Br/Br...C, (f) C...O/O...C, (g) Br...Br, (h) O...Br/Br...O, and (i) O...O contacts.

Hirshfeld surface. Not surprisingly, H...H contacts are the major contributor (43.1%), while the Br...H/H...Br contacts (18.2%) are present as a relatively large contributor, on the same level as C...H/H...C contacts (19.5%). O...H/H...O (10.3%), C...Br/Br...C (4.6%), C...O/O...C (1.7%), Br...Br (1.1%), and O...Br/Br...O (0.7%) contacts also make significant contributions to the Hirshfeld surface.

6. Synthesis and crystallization

To a 10 ml flask, 4-bromobenzoyl chloride (6.0 mmol, 1.32 g), TiCl₄ (18 mmol, 3.41 g) and methylene dichloride (3.6 ml) were placed and stirred at 273 K. To reaction mixture thus obtained, 2,7-diethoxynaphthalene (2.0 mmol, 433 mg) was added. After the reaction mixture was stirred at 298 K for 24 h, it was poured into ice-cold water (30 ml). The aqueous layer was extracted with CHCl₃ (20 ml, three times). The combined extracts were washed with 2 M aqueous NaOH followed by washing with brine. The organic layers thus obtained were dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to give a cake (96% crude yield). The crude product was purified by reprecipitation (CHCl₃/methanol; isolated yield 77%). Finally, the isolated product was crystallized from methanol to give single crystals.

¹H NMR (300 MHz, CDCl₃): 0.962 (6H, t, $J = 6.9$ Hz), 3.97 (4H, q, $J = 6.9$ Hz), 7.16 (2H, d, $J = 9.0$ Hz), 7.50 (4H, d, $J = 8.1$ Hz), 7.59 (4H, d, $J = 8.7$ Hz), 7.93 (2H, d, $J = 9.0$ Hz) ppm; ¹³C NMR (75 MHz, CDCl₃): 14.5, 65.0, 112.19, 121.02, 125.53, 127.67, 130.42, 130.58, 131.35, 132.54, 138.17, 156.13, 196.83 ppm; IR (KBr): 1658 (C=O), 1608, 1584, 1509 (Ar, naphthalene), 1274, 1112 (C—O—C) cm⁻¹; HRMS (FAB): calculated for C₂₈H₂₃Br₂O₄ [$M + H$]⁺, 580.9958, found, 580.9963; m.p. = 491–492 K.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were located in difference-Fourier maps and were subsequently refined as riding atoms, with C—H = 0.95 (aromatic), 0.98 (methyl) and 0.99 Å (methylene), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The positions of the methyl H atoms were rotationally optimized.

Acknowledgements

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Table 2

Experimental details.

Crystal data	
Chemical formula	C ₂₈ H ₂₂ Br ₂ O ₄
<i>M_r</i>	582.27
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	193
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.74560 (14), 24.4234 (4), 13.0590 (2)
β (°)	101.6109 (9)
<i>V</i> (Å ³)	2419.86 (8)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ^{−1})	4.52
Crystal size (mm)	0.60 × 0.30 × 0.10
Data collection	
Diffractionmeter	Rigaku R-Axis RAPID
Absorption correction	Numerical (NUMABS; Rigaku, 1999)
<i>T</i> _{min} , <i>T</i> _{max}	0.260, 0.636
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	43148, 4414, 4038
<i>R</i> _{int}	0.080
(<i>sin</i> θ / λ) _{max} (Å ^{−1})	0.602
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.041, 0.113, 1.02
No. of reflections	4414
No. of parameters	331
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ^{−3})	0.97, −0.60

Computer programs: *PROCESS-AUTO* (Rigaku, 1998), *SIR2004* (Burla *et al.*, 2007), *SHELXL2019/2* (Sheldrick, 2015) and *ORTEP III* (Burnett & Johnson, 1996).

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supporting information

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Computing details

(2,7-Diethoxynaphthalene-1,8-diyl)bis[(4-bromophenyl)methanone]

Crystal data

C₂₈H₂₂Br₂O₄

M_r = 582.27

Monoclinic, *P*2₁/*c*

a = 7.74560 (14) Å

b = 24.4234 (4) Å

c = 13.0590 (2) Å

β = 101.6109 (9)°

V = 2419.86 (8) Å³

Z = 4

F(000) = 1168

D_x = 1.598 Mg m⁻³

Cu *Kα* radiation, λ = 1.54187 Å

Cell parameters from 38566 reflections

θ = 3.5–68.3°

μ = 4.52 mm⁻¹

T = 193 K

Platelet, colorless

0.60 × 0.30 × 0.10 mm

Data collection

Rigaku R-Axis RAPID

diffractometer

Detector resolution: 10.000 pixels mm⁻¹

ω scans

Absorption correction: numerical

(NUMABS; Rigaku, 1999)

T_{min} = 0.260, *T_{max}* = 0.636

43148 measured reflections

4414 independent reflections

4038 reflections with *I* > 2σ(*I*)

R_{int} = 0.080

θ_{max} = 68.3°, θ_{min} = 3.6°

h = −9→8

k = −29→29

l = −15→15

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.041

wR(*F*²) = 0.113

S = 1.02

4414 reflections

331 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0674*P*)² + 1.6111*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.003

Δρ_{max} = 0.97 e Å⁻³

Δρ_{min} = −0.60 e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.96576 (4)	1.03404 (2)	0.36431 (3)	0.05270 (14)
Br2	−0.39930 (5)	0.96823 (2)	−0.11254 (3)	0.05806 (14)
O1	0.5457 (2)	0.83055 (7)	0.50431 (13)	0.0390 (4)
O2	0.0695 (2)	0.75946 (7)	−0.00888 (13)	0.0421 (4)
O3	0.2072 (2)	0.88406 (7)	0.30927 (14)	0.0383 (4)
O4	0.3968 (2)	0.85776 (7)	0.11471 (13)	0.0366 (4)
C1	0.3978 (3)	0.80814 (9)	0.33638 (17)	0.0287 (5)
C2	0.4865 (3)	0.79004 (10)	0.43375 (18)	0.0318 (5)
C3	0.5069 (3)	0.73420 (10)	0.45840 (19)	0.0343 (5)
H3	0.573259	0.722794	0.524202	0.041*
C4	0.4296 (3)	0.69638 (10)	0.38604 (19)	0.0348 (5)
H4	0.439489	0.658560	0.403185	0.042*
C5	0.2521 (3)	0.67269 (9)	0.2143 (2)	0.0351 (5)
H5	0.260856	0.635155	0.233735	0.042*
C6	0.1602 (3)	0.68654 (10)	0.1181 (2)	0.0362 (5)
H6	0.102926	0.659242	0.071504	0.043*
C7	0.1508 (3)	0.74268 (10)	0.08802 (18)	0.0329 (5)
C8	0.2318 (3)	0.78325 (9)	0.15547 (18)	0.0307 (5)
C9	0.3223 (3)	0.76908 (9)	0.25877 (17)	0.0282 (5)
C10	0.3356 (3)	0.71244 (9)	0.28667 (19)	0.0315 (5)
C11	0.6426 (3)	0.81596 (11)	0.60611 (18)	0.0362 (5)
H11A	0.750029	0.795168	0.600616	0.043*
H11B	0.569300	0.793170	0.643391	0.043*
C12	0.6904 (5)	0.86904 (13)	0.6630 (2)	0.0522 (7)
C13	−0.0250 (3)	0.72077 (10)	−0.08191 (18)	0.0354 (5)
H13A	−0.112423	0.700710	−0.050432	0.043*
H13B	0.057209	0.693956	−0.102999	0.043*
C14	−0.1154 (4)	0.75342 (13)	−0.1744 (2)	0.0413 (6)
C15	0.3600 (3)	0.86834 (9)	0.32537 (17)	0.0295 (5)
C16	0.5085 (3)	0.90805 (9)	0.33684 (17)	0.0288 (5)
C17	0.4838 (4)	0.96148 (10)	0.3671 (2)	0.0356 (6)
H17	0.372901	0.972407	0.380858	0.043*
C18	0.6210 (3)	0.99900 (10)	0.3774 (2)	0.0397 (6)
H18	0.606068	1.035412	0.399668	0.048*
C19	0.7794 (3)	0.98247 (10)	0.35463 (19)	0.0354 (5)
C20	0.8064 (3)	0.92963 (10)	0.3238 (2)	0.0379 (5)
H20	0.916284	0.919065	0.308167	0.046*
C21	0.6708 (3)	0.89269 (10)	0.31622 (19)	0.0346 (5)
H21	0.688291	0.855973	0.296535	0.042*
C22	0.2491 (3)	0.83933 (9)	0.11044 (17)	0.0306 (5)
C23	0.0907 (3)	0.87051 (9)	0.05858 (18)	0.0316 (5)
C24	0.1076 (4)	0.90948 (10)	−0.0163 (2)	0.0393 (6)
H24	0.219855	0.916307	−0.032517	0.047*
C25	−0.0379 (4)	0.93838 (11)	−0.0673 (2)	0.0450 (6)
H25	−0.027117	0.964235	−0.120001	0.054*

C26	−0.1990 (4)	0.92916 (10)	−0.04062 (19)	0.0397 (6)
C27	−0.2194 (4)	0.89222 (10)	0.0362 (2)	0.0389 (6)
H27	−0.330361	0.887427	0.055432	0.047*
C28	−0.0730 (3)	0.86228 (10)	0.08457 (19)	0.0359 (5)
H28	−0.084796	0.835830	0.136056	0.043*
H12A	0.755 (6)	0.8901 (17)	0.620 (3)	0.087 (13)*
H12B	0.767 (5)	0.8628 (16)	0.729 (3)	0.077 (11)*
H12C	0.582 (6)	0.8867 (16)	0.675 (3)	0.076 (12)*
H14A	−0.198 (4)	0.7801 (14)	−0.161 (3)	0.054 (9)*
H14B	−0.175 (5)	0.7325 (17)	−0.223 (3)	0.067 (11)*
H14C	−0.028 (5)	0.7722 (14)	−0.202 (3)	0.060 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0453 (2)	0.03872 (19)	0.0717 (2)	−0.01329 (11)	0.00611 (17)	0.00497 (12)
Br2	0.0582 (3)	0.0595 (2)	0.0506 (2)	0.02283 (14)	−0.00315 (16)	0.00419 (13)
O1	0.0469 (11)	0.0367 (9)	0.0299 (8)	−0.0034 (7)	−0.0007 (7)	0.0020 (7)
O2	0.0493 (11)	0.0352 (9)	0.0360 (9)	−0.0048 (8)	−0.0054 (8)	−0.0029 (7)
O3	0.0252 (9)	0.0425 (9)	0.0469 (10)	0.0039 (7)	0.0071 (7)	−0.0026 (7)
O4	0.0310 (10)	0.0418 (9)	0.0377 (9)	−0.0062 (7)	0.0085 (7)	−0.0011 (7)
C1	0.0221 (12)	0.0327 (11)	0.0327 (11)	−0.0016 (9)	0.0086 (9)	0.0015 (9)
C2	0.0254 (12)	0.0374 (12)	0.0328 (11)	−0.0029 (9)	0.0065 (9)	−0.0003 (9)
C3	0.0318 (13)	0.0382 (12)	0.0327 (12)	−0.0005 (10)	0.0056 (10)	0.0055 (9)
C4	0.0302 (13)	0.0338 (12)	0.0409 (13)	0.0009 (10)	0.0084 (10)	0.0061 (10)
C5	0.0339 (13)	0.0271 (11)	0.0453 (13)	−0.0013 (9)	0.0106 (11)	−0.0005 (9)
C6	0.0330 (14)	0.0310 (12)	0.0439 (13)	−0.0036 (10)	0.0064 (10)	−0.0055 (10)
C7	0.0281 (13)	0.0351 (12)	0.0350 (12)	−0.0013 (9)	0.0048 (10)	−0.0001 (9)
C8	0.0259 (12)	0.0313 (11)	0.0352 (12)	0.0001 (9)	0.0067 (9)	−0.0007 (9)
C9	0.0206 (12)	0.0311 (11)	0.0339 (12)	−0.0004 (8)	0.0080 (9)	−0.0001 (8)
C10	0.0256 (12)	0.0327 (12)	0.0375 (12)	0.0003 (9)	0.0091 (9)	0.0009 (9)
C11	0.0301 (13)	0.0476 (14)	0.0291 (11)	−0.0005 (10)	0.0022 (10)	0.0016 (10)
C12	0.055 (2)	0.0529 (17)	0.0416 (15)	−0.0069 (14)	−0.0068 (14)	−0.0029 (13)
C13	0.0327 (13)	0.0400 (13)	0.0338 (12)	−0.0068 (10)	0.0072 (10)	−0.0075 (10)
C14	0.0359 (15)	0.0530 (16)	0.0345 (13)	−0.0089 (13)	0.0062 (11)	−0.0027 (11)
C15	0.0262 (13)	0.0355 (12)	0.0269 (10)	0.0018 (9)	0.0059 (9)	−0.0022 (8)
C16	0.0270 (12)	0.0307 (11)	0.0277 (10)	0.0024 (9)	0.0029 (9)	0.0011 (8)
C17	0.0323 (14)	0.0342 (13)	0.0406 (14)	0.0046 (9)	0.0086 (11)	−0.0010 (9)
C18	0.0422 (15)	0.0286 (11)	0.0471 (14)	0.0029 (10)	0.0061 (11)	−0.0024 (10)
C19	0.0324 (13)	0.0320 (11)	0.0389 (13)	−0.0049 (10)	0.0001 (10)	0.0056 (10)
C20	0.0273 (13)	0.0363 (13)	0.0498 (14)	0.0010 (10)	0.0068 (10)	−0.0005 (10)
C21	0.0294 (13)	0.0304 (11)	0.0436 (13)	0.0024 (9)	0.0067 (10)	−0.0019 (9)
C22	0.0323 (13)	0.0335 (11)	0.0264 (11)	−0.0034 (9)	0.0068 (9)	−0.0030 (9)
C23	0.0331 (13)	0.0307 (11)	0.0301 (11)	−0.0013 (9)	0.0044 (9)	−0.0020 (9)
C24	0.0410 (15)	0.0389 (13)	0.0399 (13)	−0.0007 (11)	0.0124 (11)	0.0044 (10)
C25	0.0573 (18)	0.0395 (13)	0.0396 (14)	0.0059 (12)	0.0129 (12)	0.0093 (11)
C26	0.0428 (15)	0.0376 (13)	0.0355 (12)	0.0097 (11)	0.0001 (11)	−0.0015 (10)
C27	0.0330 (14)	0.0442 (13)	0.0386 (13)	0.0004 (11)	0.0051 (10)	−0.0018 (10)

C28	0.0351 (14)	0.0384 (12)	0.0337 (12)	−0.0024 (10)	0.0057 (10)	0.0042 (10)
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Geometric parameters (Å, °)

Br1—C19	1.901 (2)	C12—H12C	0.99 (4)
Br2—C26	1.901 (3)	C13—C14	1.498 (4)
O1—C2	1.367 (3)	C13—H13A	0.9900
O1—C11	1.434 (3)	C13—H13B	0.9900
O2—C7	1.358 (3)	C14—H14A	0.95 (4)
O2—C13	1.434 (3)	C14—H14B	0.87 (4)
O3—C15	1.221 (3)	C14—H14C	0.94 (4)
O4—C22	1.220 (3)	C15—C16	1.489 (3)
C1—C2	1.390 (3)	C16—C17	1.388 (3)
C1—C9	1.428 (3)	C16—C21	1.389 (3)
C1—C15	1.501 (3)	C17—C18	1.390 (4)
C2—C3	1.403 (3)	C17—H17	0.9500
C3—C4	1.370 (3)	C18—C19	1.379 (4)
C3—H3	0.9500	C18—H18	0.9500
C4—C10	1.410 (3)	C19—C20	1.381 (3)
C4—H4	0.9500	C20—C21	1.373 (3)
C5—C6	1.357 (4)	C20—H20	0.9500
C5—C10	1.417 (3)	C21—H21	0.9500
C5—H5	0.9500	C22—C23	1.486 (3)
C6—C7	1.424 (3)	C23—C24	1.389 (3)
C6—H6	0.9500	C23—C28	1.392 (4)
C7—C8	1.389 (3)	C24—C25	1.382 (4)
C8—C9	1.432 (3)	C24—H24	0.9500
C8—C22	1.507 (3)	C25—C26	1.380 (4)
C9—C10	1.429 (3)	C25—H25	0.9500
C11—C12	1.503 (4)	C26—C27	1.382 (4)
C11—H11A	0.9900	C27—C28	1.390 (4)
C11—H11B	0.9900	C27—H27	0.9500
C12—H12A	0.97 (5)	C28—H28	0.9500
C12—H12B	0.96 (4)		
C2—O1—C11	119.16 (19)	H13A—C13—H13B	108.7
C7—O2—C13	119.96 (19)	C13—C14—H14A	116 (2)
C2—C1—C9	119.5 (2)	C13—C14—H14B	112 (3)
C2—C1—C15	116.8 (2)	H14A—C14—H14B	105 (3)
C9—C1—C15	122.8 (2)	C13—C14—H14C	108 (2)
O1—C2—C1	115.1 (2)	H14A—C14—H14C	107 (3)
O1—C2—C3	122.8 (2)	H14B—C14—H14C	109 (3)
C1—C2—C3	122.1 (2)	O3—C15—C16	121.0 (2)
C4—C3—C2	118.9 (2)	O3—C15—C1	119.2 (2)
C4—C3—H3	120.5	C16—C15—C1	119.8 (2)
C2—C3—H3	120.5	C17—C16—C21	119.4 (2)
C3—C4—C10	121.4 (2)	C17—C16—C15	119.5 (2)
C3—C4—H4	119.3	C21—C16—C15	121.0 (2)

C10—C4—H4	119.3	C16—C17—C18	120.0 (2)
C6—C5—C10	122.1 (2)	C16—C17—H17	120.0
C6—C5—H5	119.0	C18—C17—H17	120.0
C10—C5—H5	119.0	C19—C18—C17	118.9 (2)
C5—C6—C7	118.9 (2)	C19—C18—H18	120.6
C5—C6—H6	120.5	C17—C18—H18	120.6
C7—C6—H6	120.5	C18—C19—C20	122.0 (2)
O2—C7—C8	116.2 (2)	C18—C19—Br1	119.22 (18)
O2—C7—C6	122.4 (2)	C20—C19—Br1	118.8 (2)
C8—C7—C6	121.4 (2)	C21—C20—C19	118.5 (2)
C7—C8—C9	119.9 (2)	C21—C20—H20	120.8
C7—C8—C22	117.7 (2)	C19—C20—H20	120.8
C9—C8—C22	121.5 (2)	C20—C21—C16	121.2 (2)
C1—C9—C10	117.9 (2)	C20—C21—H21	119.4
C1—C9—C8	124.1 (2)	C16—C21—H21	119.4
C10—C9—C8	118.1 (2)	O4—C22—C23	120.8 (2)
C4—C10—C5	120.3 (2)	O4—C22—C8	118.3 (2)
C4—C10—C9	120.1 (2)	C23—C22—C8	120.9 (2)
C5—C10—C9	119.6 (2)	C24—C23—C28	119.3 (2)
O1—C11—C12	106.0 (2)	C24—C23—C22	119.1 (2)
O1—C11—H11A	110.5	C28—C23—C22	121.6 (2)
C12—C11—H11A	110.5	C25—C24—C23	120.4 (2)
O1—C11—H11B	110.5	C25—C24—H24	119.8
C12—C11—H11B	110.5	C23—C24—H24	119.8
H11A—C11—H11B	108.7	C26—C25—C24	119.1 (2)
C11—C12—H12A	106 (2)	C26—C25—H25	120.5
C11—C12—H12B	111 (2)	C24—C25—H25	120.5
H12A—C12—H12B	108 (3)	C25—C26—C27	122.1 (2)
C11—C12—H12C	109 (2)	C25—C26—Br2	118.88 (19)
H12A—C12—H12C	114 (3)	C27—C26—Br2	119.0 (2)
H12B—C12—H12C	109 (3)	C26—C27—C28	118.1 (2)
O2—C13—C14	106.2 (2)	C26—C27—H27	120.9
O2—C13—H13A	110.5	C28—C27—H27	120.9
C14—C13—H13A	110.5	C27—C28—C23	120.9 (2)
O2—C13—H13B	110.5	C27—C28—H28	119.6
C14—C13—H13B	110.5	C23—C28—H28	119.6
C11—O1—C2—C1	−178.5 (2)	C2—C1—C15—O3	−114.3 (2)
C11—O1—C2—C3	4.0 (3)	C9—C1—C15—O3	54.9 (3)
C9—C1—C2—O1	−176.65 (19)	C2—C1—C15—C16	64.1 (3)
C15—C1—C2—O1	−7.0 (3)	C9—C1—C15—C16	−126.6 (2)
C9—C1—C2—C3	0.9 (3)	O3—C15—C16—C17	23.4 (3)
C15—C1—C2—C3	170.5 (2)	C1—C15—C16—C17	−155.0 (2)
O1—C2—C3—C4	174.1 (2)	O3—C15—C16—C21	−155.7 (2)
C1—C2—C3—C4	−3.3 (4)	C1—C15—C16—C21	25.9 (3)
C2—C3—C4—C10	2.2 (4)	C21—C16—C17—C18	−0.5 (4)
C10—C5—C6—C7	1.5 (4)	C15—C16—C17—C18	−179.5 (2)
C13—O2—C7—C8	−176.9 (2)	C16—C17—C18—C19	1.5 (4)

C13—O2—C7—C6	5.8 (4)	C17—C18—C19—C20	−1.1 (4)
C5—C6—C7—O2	176.3 (2)	C17—C18—C19—Br1	178.12 (18)
C5—C6—C7—C8	−0.8 (4)	C18—C19—C20—C21	−0.3 (4)
O2—C7—C8—C9	−179.3 (2)	Br1—C19—C20—C21	−179.53 (19)
C6—C7—C8—C9	−2.0 (4)	C19—C20—C21—C16	1.3 (4)
O2—C7—C8—C22	−10.2 (3)	C17—C16—C21—C20	−1.0 (4)
C6—C7—C8—C22	167.1 (2)	C15—C16—C21—C20	178.1 (2)
C2—C1—C9—C10	2.5 (3)	C7—C8—C22—O4	−118.5 (2)
C15—C1—C9—C10	−166.5 (2)	C9—C8—C22—O4	50.5 (3)
C2—C1—C9—C8	−178.6 (2)	C7—C8—C22—C23	59.3 (3)
C15—C1—C9—C8	12.5 (3)	C9—C8—C22—C23	−131.8 (2)
C7—C8—C9—C1	−175.0 (2)	O4—C22—C23—C24	23.3 (3)
C22—C8—C9—C1	16.3 (3)	C8—C22—C23—C24	−154.3 (2)
C7—C8—C9—C10	4.0 (3)	O4—C22—C23—C28	−155.5 (2)
C22—C8—C9—C10	−164.7 (2)	C8—C22—C23—C28	26.8 (3)
C3—C4—C10—C5	−178.0 (2)	C28—C23—C24—C25	−2.4 (4)
C3—C4—C10—C9	1.2 (4)	C22—C23—C24—C25	178.8 (2)
C6—C5—C10—C4	179.8 (2)	C23—C24—C25—C26	1.9 (4)
C6—C5—C10—C9	0.5 (4)	C24—C25—C26—C27	0.5 (4)
C1—C9—C10—C4	−3.5 (3)	C24—C25—C26—Br2	−179.1 (2)
C8—C9—C10—C4	177.4 (2)	C25—C26—C27—C28	−2.5 (4)
C1—C9—C10—C5	175.8 (2)	Br2—C26—C27—C28	177.15 (18)
C8—C9—C10—C5	−3.3 (3)	C26—C27—C28—C23	2.0 (4)
C2—O1—C11—C12	179.0 (2)	C24—C23—C28—C27	0.4 (4)
C7—O2—C13—C14	173.3 (2)	C22—C23—C28—C27	179.2 (2)

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

$Cg2$, $Cg3$ and $Cg5$ are the centroids of the C5—C10, C16—C21 and C1—C10 rings, respectively.

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C20—H20 $\cdots$ O3 ⁱ	0.95	2.41	3.339 (3)	167
C27—H27 $\cdots$ O4 ⁱⁱ	0.95	2.50	3.439 (3)	170
C11—H11B $\cdots$ Cg2 ⁱⁱⁱ	0.99	2.75	3.632 (3)	148
C11—H13B $\cdots$ Cg5 ⁱⁱⁱ	0.99	2.89	3.838 (3)	162
C14—H14C $\cdots$ Cg2 ^{iv}	0.98	2.78 (4)	3.631 (3)	151 (3)
C14—H14C $\cdots$ Cg5 ^{iv}	0.98	2.85 (4)	3.632 (3)	141 (3)
C12—H12A $\cdots$ Br1 ^v	0.97 (4)	2.82 (5)	3.634 (4)	141 (3)
C26—Br2 $\cdots$ Cg3 ^{vi}	1.90 (1)	3.88 (1)	5.626 (3)	152 (1)

Symmetry codes: (i) $x+1, y, z$; (ii) $x-1, y, z$; (iii) $x, -y+3/2, z+1/2$; (iv) $x, -y+3/2, z-1/2$; (v) $-x+2, -y+2, -z+1$; (vi) $-x, -y+2, -z$.