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The crystal structure of (2,7-dimethoxynaphthalene-1,8-diyl) bis((3-nitrophenyl)methanone), $C_{26}H_{18}N_2O_8$

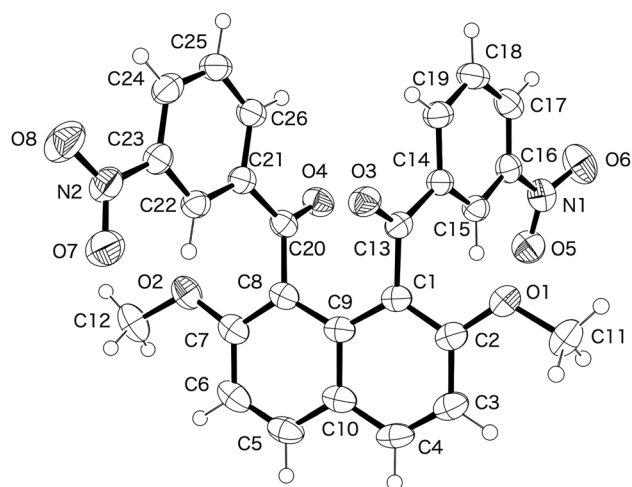


Table 1: Data collection and handling.

Crystal:	Yellow platelet
Size:	0.45 × 0.30 × 0.10 mm
Wavelength:	Cu K α radiation (1.54187 Å)
μ :	0.96 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} :	19384, 3867, 0.028
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3171
$N(\text{param})_{\text{refined}}$:	327
Programs:	Rigaku, ^{1,2} SIR2004, ³ SHELXL-2019/2, ⁴ ORTEPIII, ⁵ PLATON ⁶

1 Source of materials

Title compound was prepared via electrophilic aromatic substitution of 2,7-dimethoxynaphthalene with reference to literature.⁷ To a solution of 3-nitrobenzoyl chloride (223 mg, 1.2 mmol) in 1,2-dichloroethane (0.5 mL), TiCl₄ (341 mg, 1.8 mmol) was added and stirred at 60 °C for 30 min. To the resulting solution was added 2,7-dimethoxynaphthalene (37.6 mg, 0.20 mmol) and stirred at 60 °C for 3 h. The reaction mixture was poured into iced water (30 mL) and the obtained mixture was extracted with chloroform for five times (20 mL × 5). The combined extracts were washed with 2 M NaOH aq. for three times (20 mL × 3) to separate the residual acyl chloride and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure followed by washing with acetone to give a cake of the crude material (87 % yield). Yellow platelet single crystals were obtained by crystallization from acetone (14 %). ¹H NMR δ (300 MHz, CDCl₃): 3.71 (6H, s), 7.26 (2H, d, J = 9.0 Hz), 7.62 (2H, dd, J = 7.8, 7.8 Hz), 8.06 (2H, d, J = 9.0 Hz), 8.07 (2H, d (broad), J = 8.1 Hz), 8.41 (2H, d (broad), J = 9.3 Hz), 8.53 (2H, dd, J = 1.8, 1.8 Hz) ppm. ¹³C NMR δ (125 MHz, CDCl₃): 56.48, 111.26, 119.43, 124.06, 125.68, 127.21, 129.35, 133.52, 134.63, 138.75, 140.20, 148.78, 157.15, 196.10 ppm. IR (KBr): 1672 (C=O), 1614, 1530, 1512 (Ar, naphthalene), 1350 (N=O), 1266 (O–Me) cm⁻¹. Elemental analysis: Calcd. for C₂₆H₁₈N₂O₈: C, 64.20 %; H, 3.73 % found: C, 64.17 %; H, 3.73 %. m.p. = 292–294 °C.

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Abstract

C₂₆H₁₈N₂O₈, triclinic, $P\bar{1}$ (no. 2), a = 8.41284(15) Å, b = 10.9410(2) Å, c = 12.9659(2) Å, α = 114.567(1)°, β = 97.779(1)°, γ = 91.504(1)°, V = 1070.90(3) Å³, Z = 2, $R_{\text{gt}}(F)$ = 0.0382, $wR_{\text{ref}}(F^2)$ = 0.1083, T = 193 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.45365 (13)	0.68012 (11)	0.72846 (9)	0.0431 (3)
O2	0.07361 (14)	0.97874 (12)	1.22782 (10)	0.0488 (3)
O3	0.44838 (12)	0.64216 (11)	0.97527 (9)	0.0402 (3)
O4	0.05123 (12)	0.67224 (11)	1.00083 (9)	0.0423 (3)
O5	−0.12696 (14)	0.52600 (13)	0.57695 (10)	0.0524 (3)
O6	−0.14651 (15)	0.30780 (14)	0.48925 (11)	0.0637 (4)
O7	0.61609 (16)	0.96697 (13)	1.40985 (10)	0.0584 (4)
O8	0.64411 (16)	0.82615 (15)	1.48666 (11)	0.0647 (4)
N1	−0.08781 (16)	0.41493 (15)	0.56830 (11)	0.0443 (3)
N2	0.57945 (17)	0.85930 (15)	1.41309 (12)	0.0464 (3)
C1	0.33025 (16)	0.77742 (15)	0.89023 (12)	0.0331 (3)
C2	0.39378 (17)	0.79232 (16)	0.80222 (13)	0.0360 (3)
C3	0.40065 (18)	0.91637 (17)	0.79456 (14)	0.0416 (4)
H3	0.441687	0.924378	0.732675	0.050*
C4	0.34817 (19)	1.02457 (17)	0.87631 (14)	0.0431 (4)
H4	0.357029	1.109209	0.872356	0.052*
C5	0.22187 (19)	1.12871 (16)	1.04924 (15)	0.0448 (4)
H5	0.228832	1.212129	1.043024	0.054*
C6	0.15542 (19)	1.12208 (16)	1.13696 (15)	0.0451 (4)
H6	0.117468	1.199932	1.191550	0.054*
C7	0.14357 (18)	0.99756 (16)	1.14582 (13)	0.0391 (4)
C8	0.19788 (17)	0.88364 (15)	1.06708 (12)	0.0341 (3)
C9	0.26919 (16)	0.88944 (15)	0.97505 (12)	0.0334 (3)
C10	0.28054 (18)	1.01595 (15)	0.96750 (13)	0.0391 (4)
C11	0.5194 (2)	0.68806 (19)	0.63527 (14)	0.0479 (4)
H11A	0.434389	0.704684	0.584261	0.057*
H11B	0.563567	0.602875	0.592206	0.057*
H11C	0.605259	0.762085	0.665376	0.057*
C12	0.0197 (2)	1.09272 (18)	1.31563 (15)	0.0541 (5)
H12A	−0.028896	1.063599	1.367233	0.065*
H12B	−0.060569	1.133084	1.280306	0.065*
H12C	0.111454	1.159564	1.359502	0.065*
C13	0.34910 (17)	0.64623 (15)	0.89961 (12)	0.0323 (3)
C14	0.24392 (17)	0.52227 (15)	0.81708 (12)	0.0327 (3)
C15	0.13116 (17)	0.52594 (15)	0.72992 (12)	0.0343 (3)
H15	0.120703	0.606706	0.719855	0.041*
C16	0.03463 (17)	0.40936 (16)	0.65824 (12)	0.0366 (3)
C17	0.04471 (19)	0.29023 (16)	0.67005 (14)	0.0426 (4)
H17	−0.022400	0.211302	0.618682	0.051*
C18	0.1552 (2)	0.28860 (16)	0.75875 (14)	0.0435 (4)
H18	0.162738	0.208199	0.769711	0.052*
C19	0.25503 (19)	0.40359 (16)	0.83169 (13)	0.0382 (3)
H19	0.331291	0.401351	0.891881	0.046*
C20	0.15724 (16)	0.75151 (15)	1.07253 (12)	0.0336 (3)
C21	0.24974 (17)	0.71621 (15)	1.16148 (12)	0.0334 (3)
C22	0.36556 (17)	0.80728 (16)	1.24840 (12)	0.0352 (3)
H22	0.383797	0.896896	1.255974	0.042*
C23	0.45372 (18)	0.76522 (16)	1.32363 (13)	0.0377 (3)
C24	0.43233 (19)	0.63490 (17)	1.31442 (13)	0.0415 (4)
H24	0.495120	0.608074	1.366768	0.050*
C25	0.3174 (2)	0.54474 (16)	1.22720 (14)	0.0427 (4)
H25	0.300940	0.454799	1.219208	0.051*
C26	0.22621 (19)	0.58480 (16)	1.15151 (13)	0.0385 (4)
H26	0.146958	0.522317	1.092292	0.046*

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

3 Comment

Understanding the nature and effectiveness of non-covalent bonding interactions in solid organic molecular substances have gained profound recognition from wide range of research fields, pharmaceutical development and manufacturing,⁸ crystal structure prediction,⁹ and crystal engineering.¹⁰ Since the intramolecular conjugation plane formation of aromatic rings is extremely hindered, crystals of compounds of non-coplanarly accumulated aromatic rings can be expected to reveal distinguished contributions of rather weak non-covalent bonding interactions¹¹ other than $\pi\cdots\pi$ stacking interactions or classical hydrogen bonds as spatial structure determining factors.

In the molecular structure of the title compound, the benzene rings of the 3-nitrobenzoyl groups at the 1,8-positions are twisted away from the naphthalene ring (see the Figure). Two 3-nitrobenzoyl groups are situated in *anti*-orientation against the naphthalene ring. On the other hand, the two benzene rings are situated in an almost parallel manner. The dihedral angles between the benzene rings of the 3-nitrobenzoyl groups and the naphthalene ring system are 72.41(6)° [C14–C19 ring, C9–C1–C13–O3 torsion angle = 67.25(19)°] and 71.88(6)° [C21–C26 ring, C9–C8–C20–O4 torsion angle = 67.17(19)°], respectively. The dihedral angle between the best planes of the two benzene rings is 1.18(7)°. The nitro groups are bound to the benzene rings in a twisted manner [dihedral angles between bridging NO₂ plane and benzene ring: O5–O6–N1–C16 plane and C1–C19 ring = 18.67(9)°; O7–O8–N2–C23 plane and C21–C26 ring = 10.11(9)°]. On the other hand, the carbonyl moieties are almost coplanar against the benzene rings [O3–C13–C14–C15 torsion angle = 179.49(14)°; O4–C20–C21–C22 torsion angle = 176.42(14)°]. In the crystal packing, five types of centrosymmetric dimeric aggregations connected by non-covalent bonding interactions are observed: type I is formed by three types of $\pi\cdots\pi$ stacking interactions between the naphthalene rings [Cg1...Cg5, 3.5068(8) Å (slippage 0.807 Å), Cg1...Cg1, 3.6337(9) Å (slippage 1.286 Å), and Cg1...Cg2, 3.7931(9) Å (slippage 1.633 Å); Cg1 = C1–C2–C3–C4–C10–C9 ring, Cg5 = C1–C2–C3–C4–C10–C5–C6–C7–C8–C9 ring, Cg2 = C5–C6–C7–C8–C9–C10 ring] and (naphthalene)C–H...O=N non-classical

hydrogen bond [H3...O7, 2.58 Å](symmetry code: 1-x, 2-y, 2-z); type II is formed by $\pi\cdots\pi$ stacking interaction between the naphthalene rings [Cg2...Cg2, 3.6383(9) Å (slippage 0.958 Å)] and (methoxy) C-H... π (naphthalene) non-classical hydrogen bond [H12B...Cg1, 2.83 Å] (symmetry code: -x, 2-y, 2-z); type III is formed by (benzene)C-H...O=C non-classical hydrogen bond [H26...O4, 2.43 Å] (symmetry code: -x, 1-y, 2-z); type IV is formed by (benzene)C-H...O=C and N=O... π (benzene) non-classical hydrogen bonds [H19...O3, 2.55 Å; O8...Cg3, 3.7376(15) Å; Cg3 = C14-C19 ring] (symmetry code: 1-x, 1-y, 2-z); type V is formed by (methoxy) C-H...O=N non-classical hydrogen bond [H11A...O6, 2.46 Å] (symmetry code: -x, 1-y, 1-z). Centrosymmetric dimeric aggregations in types I and II are built up with $\pi\cdots\pi$ stacking between naphthalene rings, whereas those in types III, IV, and V include non-classical hydrogen bonds. Interactions involving nitro groups assist both $\pi\cdots\pi$ stacking and C-H...O=C non-classical hydrogen bonds as shown in types I and IV.

The authors reported the crystal structure of the homologous compound having mono(1-aroylet) structure, (2,7-dimethoxynaphthalen-1-yl)(3-nitrophenyl)methanone (space group $P2_1/n$, $Z = 4$).¹² The monoaroylated homologue shows similar spatial situation of the aroyl group on naphthalene ring [dihedral angle between benzene ring and naphthalene ring: 69.59(5)°] with the title compound. In the crystal of the monoaroylated homologue, (benzene)C-H...O=N non-classical hydrogen bond (2.37 Å) and weak (naphthalene)C-H...O=C interactions (2.60 Å) link the molecules in translational relationship (symmetry code: x-1, y, z) along *a*-axis. The carbonyl group is connected *intramolecularly* to C-H hydrogen atom at 8-position of the naphthalene ring (C-H...O=C, 2.56 Å). Consequence of this, the nitro group plays a role to interact with the neighbouring molecule solely. On the other hand, the dual 3-nitrobenzoyl groups at the 1,8-positions on the naphthalene ring of the title compound can be used for non-covalent bonding interactions with the naphthalene ring and pairs of nitro groups, carbonyl groups, and benzene rings intermolecularly. The symmetrical arrangements of the pairs of these functional groups afford centrosymmetric dimeric aggregation structures *via* complementary non-covalent bonding interactions in multi-directions evenly well. As the 1,8-diaroylnaphthalene (*peri*-aroylnaphthalene) compounds generally have characteristic molecular structures in which aromatic rings of the molecules are situated non-coplanarly and the dihedral angles between the arene and naphthalene rings have satisfactory room to adjust the conformation of the molecule and the contact shape minutely. So the title compound, one of the *peri*-aroylnaphthalene compounds, can intermolecularly arrange the $\pi\cdots\pi$ stackings of arene rings and non-classical hydrogen bondings between Csp^3 -H

hydrogen atoms and aromatic π -systems/nitrogen atoms or Csp^2 -H hydrogen atoms and oxygen/nitrogen atoms most densely to achieve highly effective centrosymmetrical intermolecular network of non-covalent bonding interactions. This structural advantage of the title compound probably enables highly raised molecular proximity compared to the monoaroylated homologue (crystalline density 1.508 g cm⁻³ for the title compound [$P\bar{1}$]; 1.39 g cm⁻³ for the monoaroylated homologue [$P2_1/n$]).

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