

Crystal structure of *N,N'*-dibenzylpyromellitic diimide

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Received 3 November 2016

Accepted 7 November 2016

Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; pyromellitic diimide derivative; hydrogen bonding; two-dimensional network.

CCDC reference: 1515263

Supporting information: this article has supporting information at journals.iucr.org/e

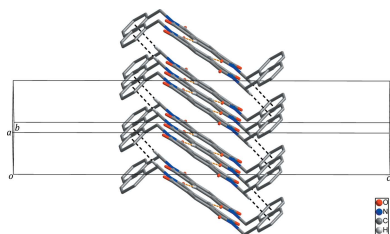
The title compound, C₂₄H₁₆N₂O₄ [systematic name: 2,6-dibenzylpyrrolo[3,4-*f*]-isoindole-1,3,5,7(2*H*,6*H*)-tetraone], consists of a central pyromellitic diimide moiety with terminal benzyl groups at the N-atom positions. The molecule is located about an inversion centre, so the asymmetric unit contains one half-molecule. In the molecule, both terminal phenyl groups, tilted by 72.97 (4)° with respect to the mean plane of the central pyromellitic diimide moiety (r.m.s. deviation = 0.0145 Å), are oriented away from each other, forming an elongated S-shaped conformation. In the crystal, molecules are connected *via* weak C—H···O hydrogen bonds and C—H···π interactions, resulting in the formation of supramolecular layers extending parallel to the *ab* plane.

1. Chemical context

As a result of their potential applications in organic photovoltaics (Huang *et al.*, 2014) and as molecular electronic devices (Guo *et al.*, 2014) and energy storage devices (Song *et al.*, 2010), several π-conjugated, redox-active aromatic diimides including pyromellitic diimides, naphthalene diimides and perylene diimides have received considerable attention from materials chemists. Additionally, π-conjugated aromatic diimides and their derivatives are used as rigid structural components in supramolecular assemblies for the exploitation of supramolecular interactions such as hydrogen-bonding and halogen–π interactions (Hay & Custelcean, 2009; Lu *et al.*, 2007; Gamez *et al.*, 2007). Recently, our group reported a copper(I) coordination polymer with a pyromellitic diimide ligand, namely *N,N'*-bis[3-(methylthio)propyl]pyromellitic diimide, and revealed the presence of halogen–π interactions between the chlorine atoms of a dichloromethane solvent molecule of crystallization and pyromellitic diimide rings (Park *et al.*, 2011). In an extension of our studies of pyromellitic diimide derivatives, we have prepared the title compound by the reaction of pyromellitic dianhydride with 2-phenylethylamine and we report its crystal structure here.

2. Structural commentary

The molecular structure of the title compound consists of a central pyromellitic diimide ring system with terminal benzyl groups on each of the inversion-related nitrogen atoms (Fig. 1). As the molecule is located about a crystallographic inversion centre, the asymmetric unit of the compound comprises one half-molecule. Short intramolecular C—H···O contacts



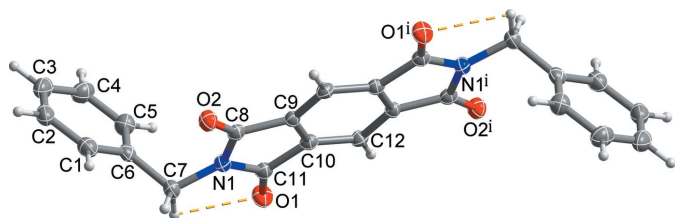
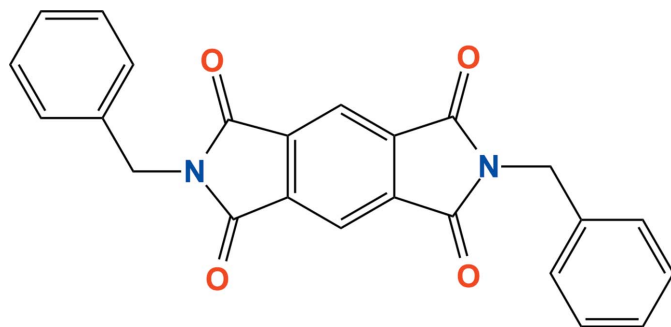


Figure 1
A view of the molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius and yellow dashed lines represent the intramolecular C–H...O short contacts. [Symmetry code; (i) $-x + 2, -y + 1, -z$.]

(Table 1) enclose $S(5)$ rings and may contribute to the planarity of the pyromellitic diimide ring system (r.m.s. deviation = 0.0145 Å). The two terminal phenyl groups in the molecule are oriented away from each other, forming an elongated S-shaped conformation. The terminal phenyl ring is tilted by $72.97(4)^\circ$ with respect to the mean plane of the central pyromellitic diimide moiety.



3. Supramolecular features

In the crystal, adjacent molecules are connected by weak C12–H12...O2 hydrogen bonds, Table 1 (yellow dashed lines in Fig. 2), forming inversion dimers. Inversion symmetry links

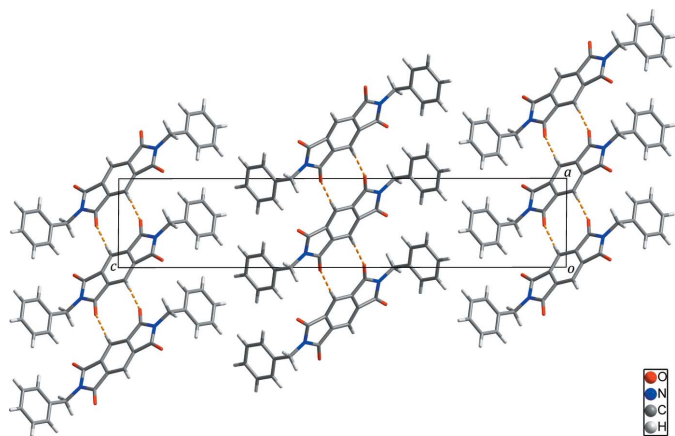


Figure 2
Chains of the title compound formed through intermolecular C–H...O hydrogen bonds (yellow dashed lines).

Table 1
Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1–C6 ring.

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------|-------|-------------|-------------|---------------|
| C7–H7B...O1 | 0.99 | 2.53 | 2.917 (2) | 103 |
| C12–H12...O2 ⁱ | 0.95 | 2.45 | 3.401 (2) | 178 |
| C7–H7B...Cg1 ⁱⁱ | 0.99 | 2.60 | 3.478 (2) | 148 |

Symmetry codes: (i) $x + 1, y + 1, z$; (ii) $x, y + 1, z$.

Table 2
Experimental details.

| | |
|--|------------------------------------|
| Crystal data | |
| Chemical formula | $C_{24}H_{16}N_2O_4$ |
| M_r | 396.39 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 173 |
| a, b, c (Å) | 6.1500 (5), 4.7475 (3), 31.002 (2) |
| β (°) | 90.461 (3) |
| V (Å ³) | 905.14 (11) |
| Z | 2 |
| Radiation type | Mo $K\alpha$ |
| μ (mm ⁻¹) | 0.10 |
| Crystal size (mm) | 0.50 × 0.06 × 0.02 |
| Data collection | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Multi-scan (SADABS; Bruker 2013) |
| T_{min}, T_{max} | 0.661, 0.746 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 4593, 2016, 1444 |
| R_{int} | 0.034 |
| $(\sin \theta/\lambda)_{max}$ (Å ⁻¹) | 0.650 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$ | 0.048, 0.119, 1.04 |
| No. of reflections | 2016 |
| No. of parameters | 136 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³) | 0.25, -0.22 |

Computer programs: APEX2 and SAINT (Bruker, 2013), SHELXS97 and SHELXTL (Sheldrick 2008), SHELXL2014 (Sheldrick, 2015) and DIAMOND (Brandenburg, 2010).

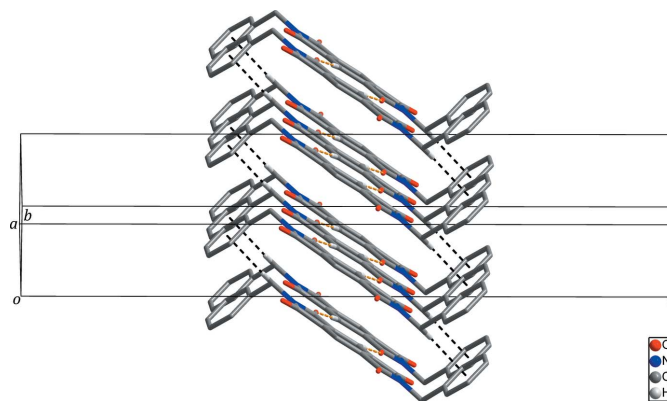


Figure 3
Supramolecular layers of the title compound formed through intermolecular C–H... π interactions (black dashed lines) between the chains generated by intermolecular C–H...O hydrogen bonds (yellow dashed lines). H atoms not involved in intermolecular interactions have been omitted for clarity.

these into a chain propagating along $[\bar{1}10]$. Neighboring chains are linked through intermolecular C—H $\cdots\pi$ interactions between a methylene H atom and the terminal phenyl ring, resulting in the formation of supramolecular layers extending parallel to the *ab* plane (black dashed lines in Fig. 3 and Table 1). These layers are separated from each other by 3.104 (3) Å. No intermolecular π – π interactions are found between the pyromellitic diimide moieties.

4. Synthesis and crystallization

The title compound was synthesized by the reaction of pyromellitic dianhydride with 2-phenylethylamine according to a literature procedure (Kang *et al.*, 2015). X-ray quality single crystals were obtained by slow evaporation of a dichloromethane solution of the title compound.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned geometrically with $d(\text{C—H}) = 0.95$ Å for $\text{Csp}^2\text{—H}$ and 0.99 Å for methylene, and were refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Acknowledgements

This work was supported from the National Research Foundation of Korea (NRF) project (2012R1A4A1027750 and 2015R1D1A3A01020410).

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supporting information

Acta Cryst. (2016). E72, 1809-1811 [https://doi.org/10.1107/S2056989016017710]

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Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

2,6-Dibenzylpyrrolo[3,4-*f*]isoindole-1,3,5,7(2*H*,6*H*)-tetraone

Crystal data

$C_{24}H_{16}N_2O_4$

$M_r = 396.39$

Monoclinic, $P2_1/n$

$a = 6.1500$ (5) Å

$b = 4.7475$ (3) Å

$c = 31.002$ (2) Å

$\beta = 90.461$ (3)°

$V = 905.14$ (11) Å³

$Z = 2$

$F(000) = 412$

$D_x = 1.454$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 874 reflections

$\theta = 2.6$ – 24.8 °

$\mu = 0.10$ mm⁻¹

$T = 173$ K

Needle, colourless

$0.50 \times 0.06 \times 0.02$ mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker 2013)

$T_{\min} = 0.661$, $T_{\max} = 0.746$

4593 measured reflections

2016 independent reflections

1444 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 1.3$ °

$h = -6$ → 7

$k = -2$ → 6

$l = -38$ → 40

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.119$

$S = 1.04$

2016 reflections

136 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.089P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.25$ e Å⁻³

$\Delta\rho_{\min} = -0.22$ 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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|------------|-------------|----------------------------------|
| O1 | 0.9145 (2) | 0.9617 (3) | 0.09759 (4) | 0.0314 (4) |
| O2 | 0.4737 (2) | 0.2514 (3) | 0.04921 (4) | 0.0282 (3) |
| N1 | 0.6589 (2) | 0.6176 (3) | 0.08217 (5) | 0.0218 (4) |
| C1 | 0.2783 (3) | 0.3279 (4) | 0.15445 (6) | 0.0303 (5) |
| H1 | 0.1617 | 0.3659 | 0.1350 | 0.036* |
| C2 | 0.2505 (4) | 0.1311 (4) | 0.18711 (7) | 0.0363 (5) |
| H2 | 0.1157 | 0.0354 | 0.1901 | 0.044* |
| C3 | 0.4206 (4) | 0.0760 (4) | 0.21524 (7) | 0.0399 (6) |
| H3 | 0.4021 | -0.0568 | 0.2378 | 0.048* |
| C4 | 0.6175 (4) | 0.2130 (4) | 0.21071 (6) | 0.0356 (5) |
| H4 | 0.7346 | 0.1724 | 0.2299 | 0.043* |
| C5 | 0.6439 (3) | 0.4094 (4) | 0.17812 (6) | 0.0298 (5) |
| H5 | 0.7792 | 0.5036 | 0.1751 | 0.036* |
| C6 | 0.4739 (3) | 0.4699 (4) | 0.14973 (6) | 0.0233 (4) |
| C7 | 0.4994 (3) | 0.6895 (4) | 0.11523 (6) | 0.0252 (4) |
| H7A | 0.3565 | 0.7201 | 0.1011 | 0.030* |
| H7B | 0.5432 | 0.8691 | 0.1290 | 0.030* |
| C8 | 0.8499 (3) | 0.7687 (3) | 0.07548 (6) | 0.0213 (4) |
| C9 | 0.9507 (3) | 0.6455 (3) | 0.03618 (5) | 0.0199 (4) |
| C10 | 0.8168 (3) | 0.4283 (3) | 0.02169 (5) | 0.0186 (4) |
| C11 | 0.6279 (3) | 0.4093 (3) | 0.05118 (5) | 0.0211 (4) |
| C12 | 1.1389 (3) | 0.7249 (3) | 0.01520 (5) | 0.0202 (4) |
| H12 | 1.2303 | 0.8725 | 0.0253 | 0.024* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|--------------|-------------|--------------|
| O1 | 0.0344 (9) | 0.0305 (7) | 0.0293 (7) | -0.0060 (6) | 0.0023 (6) | -0.0098 (6) |
| O2 | 0.0247 (8) | 0.0285 (7) | 0.0316 (7) | -0.0056 (6) | 0.0030 (6) | -0.0014 (6) |
| N1 | 0.0230 (9) | 0.0219 (7) | 0.0204 (8) | 0.0001 (6) | 0.0034 (6) | -0.0008 (6) |
| C1 | 0.0264 (11) | 0.0300 (9) | 0.0346 (11) | 0.0002 (8) | 0.0036 (9) | -0.0041 (9) |
| C2 | 0.0402 (14) | 0.0287 (10) | 0.0401 (12) | -0.0023 (10) | 0.0169 (10) | -0.0015 (10) |
| C3 | 0.0580 (17) | 0.0307 (10) | 0.0313 (12) | 0.0042 (11) | 0.0151 (11) | 0.0035 (9) |
| C4 | 0.0460 (14) | 0.0341 (10) | 0.0267 (10) | 0.0039 (10) | -0.0045 (9) | 0.0039 (9) |
| C5 | 0.0301 (12) | 0.0315 (9) | 0.0279 (10) | -0.0028 (9) | -0.0009 (9) | -0.0003 (9) |
| C6 | 0.0258 (11) | 0.0228 (8) | 0.0214 (9) | 0.0009 (8) | 0.0049 (8) | -0.0046 (7) |
| C7 | 0.0248 (11) | 0.0269 (9) | 0.0240 (9) | 0.0025 (8) | 0.0043 (8) | -0.0009 (8) |
| C8 | 0.0227 (10) | 0.0198 (8) | 0.0214 (9) | 0.0011 (7) | -0.0010 (8) | 0.0016 (7) |
| C9 | 0.0211 (10) | 0.0184 (8) | 0.0202 (9) | 0.0011 (7) | -0.0025 (7) | 0.0010 (7) |

| | | | | | | |
|-----|-------------|------------|------------|-------------|-------------|------------|
| C10 | 0.0187 (9) | 0.0181 (7) | 0.0190 (8) | 0.0005 (7) | 0.0001 (7) | 0.0024 (7) |
| C11 | 0.0239 (10) | 0.0194 (8) | 0.0199 (9) | 0.0012 (8) | -0.0021 (7) | 0.0027 (7) |
| C12 | 0.0229 (11) | 0.0182 (7) | 0.0195 (9) | -0.0014 (7) | -0.0019 (7) | 0.0005 (7) |

Geometric parameters (Å, °)

| | | | |
|-------------|--------------|-----------------------------|--------------|
| O1—C8 | 1.210 (2) | C4—H4 | 0.9500 |
| O2—C11 | 1.210 (2) | C5—C6 | 1.391 (2) |
| N1—C11 | 1.391 (2) | C5—H5 | 0.9500 |
| N1—C8 | 1.393 (2) | C6—C7 | 1.503 (2) |
| N1—C7 | 1.465 (2) | C7—H7A | 0.9900 |
| C1—C6 | 1.387 (3) | C7—H7B | 0.9900 |
| C1—C2 | 1.389 (3) | C8—C9 | 1.491 (2) |
| C1—H1 | 0.9500 | C9—C12 | 1.385 (2) |
| C2—C3 | 1.382 (3) | C9—C10 | 1.392 (2) |
| C2—H2 | 0.9500 | C10—C12 ⁱ | 1.384 (2) |
| C3—C4 | 1.383 (3) | C10—C11 | 1.487 (3) |
| C3—H3 | 0.9500 | C12—C10 ⁱ | 1.384 (2) |
| C4—C5 | 1.385 (3) | C12—H12 | 0.9500 |
| C11—N1—C8 | 111.98 (15) | N1—C7—C6 | 114.25 (14) |
| C11—N1—C7 | 124.05 (15) | N1—C7—H7A | 108.7 |
| C8—N1—C7 | 123.68 (14) | C6—C7—H7A | 108.7 |
| C6—C1—C2 | 121.05 (19) | N1—C7—H7B | 108.7 |
| C6—C1—H1 | 119.5 | C6—C7—H7B | 108.7 |
| C2—C1—H1 | 119.5 | H7A—C7—H7B | 107.6 |
| C3—C2—C1 | 119.4 (2) | O1—C8—N1 | 125.37 (17) |
| C3—C2—H2 | 120.3 | O1—C8—C9 | 128.58 (17) |
| C1—C2—H2 | 120.3 | N1—C8—C9 | 106.04 (14) |
| C2—C3—C4 | 120.40 (19) | C12—C9—C10 | 122.98 (16) |
| C2—C3—H3 | 119.8 | C12—C9—C8 | 129.19 (15) |
| C4—C3—H3 | 119.8 | C10—C9—C8 | 107.81 (16) |
| C3—C4—C5 | 119.9 (2) | C12 ⁱ —C10—C9 | 122.44 (16) |
| C3—C4—H4 | 120.1 | C12 ⁱ —C10—C11 | 129.49 (16) |
| C5—C4—H4 | 120.1 | C9—C10—C11 | 108.03 (15) |
| C4—C5—C6 | 120.59 (19) | O2—C11—N1 | 125.35 (18) |
| C4—C5—H5 | 119.7 | O2—C11—C10 | 128.50 (16) |
| C6—C5—H5 | 119.7 | N1—C11—C10 | 106.14 (15) |
| C1—C6—C5 | 118.72 (17) | C10 ⁱ —C12—C9 | 114.59 (15) |
| C1—C6—C7 | 120.50 (17) | C10 ⁱ —C12—H12 | 122.7 |
| C5—C6—C7 | 120.77 (17) | C9—C12—H12 | 122.7 |
| C6—C1—C2—C3 | -0.1 (3) | N1—C8—C9—C12 | 178.00 (17) |
| C1—C2—C3—C4 | -0.7 (3) | O1—C8—C9—C10 | -179.63 (17) |
| C2—C3—C4—C5 | 0.8 (3) | N1—C8—C9—C10 | -0.36 (18) |
| C3—C4—C5—C6 | -0.2 (3) | C12—C9—C10—C12 ⁱ | -0.4 (3) |
| C2—C1—C6—C5 | 0.7 (3) | C8—C9—C10—C12 ⁱ | 178.05 (15) |
| C2—C1—C6—C7 | -177.86 (17) | C12—C9—C10—C11 | -178.18 (15) |

| | | | |
|--------------|--------------|------------------------------|--------------|
| C4—C5—C6—C1 | -0.6 (3) | C8—C9—C10—C11 | 0.31 (18) |
| C4—C5—C6—C7 | 178.03 (17) | C8—N1—C11—O2 | -178.89 (16) |
| C11—N1—C7—C6 | 71.0 (2) | C7—N1—C11—O2 | -4.8 (3) |
| C8—N1—C7—C6 | -115.62 (18) | C8—N1—C11—C10 | -0.08 (18) |
| C1—C6—C7—N1 | -115.50 (19) | C7—N1—C11—C10 | 173.99 (14) |
| C5—C6—C7—N1 | 65.9 (2) | C12 ⁱ —C10—C11—O2 | 1.1 (3) |
| C11—N1—C8—O1 | 179.57 (16) | C9—C10—C11—O2 | 178.61 (17) |
| C7—N1—C8—O1 | 5.5 (3) | C12 ⁱ —C10—C11—N1 | -177.67 (16) |
| C11—N1—C8—C9 | 0.27 (18) | C9—C10—C11—N1 | -0.15 (18) |
| C7—N1—C8—C9 | -173.83 (14) | C10—C9—C12—C10 ⁱ | 0.4 (3) |
| O1—C8—C9—C12 | -1.3 (3) | C8—C9—C12—C10 ⁱ | -177.73 (16) |

Symmetry code: (i) $-x+2, -y+1, -z$.

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

Cg1 is the centroid of the C1—C6 ring.

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|-------|-------------|-------------|---------------|
| C7—H7B \cdots O1 | 0.99 | 2.53 | 2.917 (2) | 103 |
| C12—H12 \cdots O2 ⁱⁱ | 0.95 | 2.45 | 3.401 (2) | 178 |
| C7—H7B \cdots Cg1 ⁱⁱⁱ | 0.99 | 2.60 | 3.478 (2) | 148 |

Symmetry codes: (ii) $x+1, y+1, z$; (iii) $x, y+1, z$.