Crystal structure of 9,9-diethyl-9H-fluorene-2,4,7-tricarbaldehyde

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The title compound, C_{20}H_{18}O_{3}, crystallizes in the space group P_{2}_1/c with one molecule in the asymmetric unit of the cell. The fluorene skeleton is nearly planar and the crystal structure is composed of molecular layers extending parallel to the (302) plane. Within a layer, one formyl oxygen atom participates in the formation of a C_{arne}—H···O bond, which is responsible for the formation of an inversion symmetric supramolecular motif of graph set R_{2}^{2}(10). A second oxygen atom is involved in an intramolecular C_{arne}—H···O hydrogen bond and is further connected with a formyl hydrogen atom of an adjacent molecule. A Hirshfeld surface analysis indicated that the most important contributions to the overall surface are from H···H (46.9%), O···H (27.9%) and C···H (17.8%) interactions.

1. Chemical context

Compounds featuring a fluorene moiety have been recognized as useful for a broad spectrum of applications, which range from agents for cell imaging, solar cells, organic light-emitting diodes to lasers. Furthermore, fluorene derivatives have the potential to act as artificial receptors for different ionic and neutral substrates in analogy to the known receptors possessing a benzene or biphenyl core, which, for example, are able to complex ammonium ions (Koch et al., 2015; Schulze et al., 2018; Chin et al., 2002; Arunachalam et al., 2010), ion pairs (Stapf et al., 2015) or carbohydrates (Stapf et al., 2020; Köhler et al., 2020, 2021; Kaiser et al., 2019; Lippe & Mazik, 2013, 2015; Amrhein et al., 2016; Amrhein & Mazik, 2021). As a result of the manifold application possibilities of fluorenes, the syntheses of new representatives of this class of compounds are the subject of intensive research (Seidel et al., 2019, 2021; Seidel & Mazik, 2020; Sicard et al., 2018). Fluorene derivatives bearing halogen, formyl or amino groups are valuable starting materials for a wide range of fluorene-based acyclic and macrocyclic compounds as well as polymers. Recently we have described the efficient one-step synthesis of 9,9-diethyl-9H-fluorene-2,4,7-tricarbaldehyde on the basis of 2,4,7-tris(bromomethyl)-9,9-diethyl-9H-fluorene (Seidel et al., 2019), which provided a threefold higher yield of the product than the previously known three-step reaction sequence (Yao & Belfield, 2005). In this work we describe the crystal structure of this fluorene derivative bearing three formyl groups.
2. Structural commentary

The title compound (I) (Fig. 1) crystallizes in the space group \( P2_1/c \) with one molecule in the asymmetric unit. The 2,4,7-substituted fluorene scaffold adopts a nearly planar geometry with the formyl groups inclined at angles of 4.2 (2), 3.5 (2) and 3.3 (2)° with respect to the fluorene moiety. These values correlate with torsion angles of \(-175.8 (3)\), \(-175.4 (3)\) and \(-176.7 (4)\)°, respectively, for the atomic sequences C3—C2—C14—O1, C3—C4—C15—O2 and C6—C7—C16—O3. The plane passing through the two ethyl groups is oriented nearly orthogonal to the plane of the fluorene unit [dihedral angle = 89.8 (1)°]. The oxygen atom O2 is involved in an intramolecular C—H···O hydrogen bond [\( d(H···O) = 2.18 \text{ Å} \), \( C—H···O 138^\circ; \text{Table 1} \).]

3. Supramolecular features

The crystal structure of the title compound is composed of molecular layers extending parallel to the (302) plane. An excerpt of the layer structure showing the mode of hydrogen bonding is depicted in Fig. 2. Within a given layer, the formyl oxygen atom O1 participates in the formation of a \( C_{\text{arene}}—H···O \) bond [\( d(H···O) = 2.59 \text{ Å} \); Table 1], thus creating an inversion-symmetric supramolecular motif of graph-set \( R_2^2(10) \) (Etter et al., 1990; Bernstein et al., 1995; for examples of other crystal structures including such a ten-membered supramolecular motif, see Seidel et al., 2021; Stapf et al., 2021). The steric requirements of the ethyl groups cause an offset of the molecules of consecutive layers, so that neither hydrogen bonds nor \( \pi–\pi \) arene stacking interactions are observed in the direction of the layer normal. Consequently, the crystal appears to be stabilized by van der Waals forces in the direction of the stacking axis of the molecular layers (Fig. 3).

4. Database Survey

A search in the Cambridge Structural Database (Version 5.41, November 2019; Groom et al., 2016) for 9\( H \)-fluorene derivatives bearing a formyl group resulted in three hits, including 9\( H \)-fluorene carbaldehyde (SAZQIT; Dobson & Gerkin, 1998) and two ferrocene-fluorene complexes including a 2-formyl-9-fluorenyl (HAPROF) and a 2,7-diformyl-9-fluorenyl moiety (HAPRUL; Wright & Cochran, 1993). As in the case of the title compound, the 9\( H \)-fluorene carbaldehyde crystallized in the space group \( P2_1/c \) with one molecule in the asymmetric unit. The molecular core is nearly planar and the crystal structure is characterized by the presence of C—H···O hydrogen bonds, which are responsible for the formation of a supramolecular motif of graph set \( R_2^2(14) \).

| \( D—H···A \) | \( D—H \) | \( H···A \) | \( D···A \) | \( D—H···A \) |
|----------------|----------|----------|----------|----------------|
| C1—H1—O1i     | 0.95     | 2.59     | 3.512 (4) | 165            |
| C5—H5—O2      | 0.95     | 2.18     | 2.961 (4) | 138            |
| C5—H5—O3ii    | 0.95     | 2.67     | 3.350 (4) | 129            |
| C16—H16—O2iii | 0.95     | 2.53     | 3.321 (4) | 141            |
| C17—H17A—O1iii| 0.99     | 2.68     | 3.611 (4) | 157            |

Symmetry codes: (i) \( x+1, y+1, z+1 \); (ii) \( x, y, z+1 \); (iii) \( x, y+1, z+1 \).
5. Hirshfeld surface analysis

Hirshfeld surfaces (Spackman & Jayatilaka, 2009) were calculated and the associated 2D fingerprint plots generated using Crystal Explorer 17.5 (Turner et al., 2017). The 2D fingerprint plots (McKinnon et al., 2007) are displayed within the expanded 0.4–3.0 Å range including reciprocal contacts (Fig. 4); 3D \( d_{\text{norm}} \) surfaces are mapped over a fixed colour scale of ~0.3 a.u. (red)–1.0 a.u. (blue) (Figs. 5 and 6). The 2D fingerprint plots (see Fig. 4) indicate that the most important contributions to the overall surface are from H⋯H (46.9%), O⋯H (27.9%) and C⋯C (17.8%) interactions, whereas only 3.8% and 2.6% are from the C⋯C and C⋯O contacts, respectively. In addition to the fingerprint plots, the Hirshfeld plots mapped with \( d_{\text{norm}} \) give a hint about the significance of the close contacts. For example, the O⋯H hydrogen bonds are responsible for the intense red spots on the surface, as shown in Figs. 5 and 6.

6. Synthesis and crystallization

The title compound was prepared by an efficient one-step synthesis involving the treatment of 2,4,7-tris(bromomethyl)-9,9-diethyl-9\( H \)-fluorene with N-methylmorpholine N-oxide (Seidel et al., 2019). Single crystals of (I) were achieved via crystallization from a mixture of dichloromethane and \( n \)-hexane (1:1 v/v).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms: C—H = 0.95 Å for aryl-H atoms, C—H = 0.99 Å for methylene groups and C—H = 0.98 Å for methyl groups with \( U_{\text{iso}}(H) \) = \( 1.5U_{\text{eq}}(C) \) for methyl groups and \( U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C) \) for other hydrogen atoms. The crystal structure of (I) was refined as a two-component twin with an approximate occupancy ratio of 63:37.

Acknowledgements

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Table 2
Experimental details.

| Parameter                      | Value            |
|--------------------------------|------------------|
| Chemical formula               | C_{20}H_{18}O_{3} |
| M<sub>v</sub>                  | 306.34           |
| Crystal system, space group    | Monoclinic, P2₁/c |
| Temperature (K)                | 150              |
| a, b, c (Å)                    | 15.6595 (9), 13.1466 (14), 7.6834 (15) |
| β (°)                          | 93.146 (9)       |
| V (Å³)                         | 1579.4 (4)       |
| Z                              | 4                |
| Radiation type                 | Mo Kα            |
| μ (mm⁻¹)                       | 0.09             |
| Crystal size (mm)              | 0.38 x 0.30 x 0.15 |

Data collection

| Parameter                      | Value            |
|--------------------------------|------------------|
| Diffractometer                 | Stoe IPDS 2T     |
| Absorption correction –        |                  |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 13951, 13951, 8830 |
| R<sub>int</sub>                | ?                |
| (sin θ/λ)_{max} (Å⁻¹)          | 0.594            |

Refinement

| Parameter                      | Value            |
|--------------------------------|------------------|
| R(F²)                          | 0.047, 0.127, 0.93 |
| No. of reflections             | 13951            |
| No. of parameters              | 211              |
| H-atom treatment               | H-atom parameters constrained |
| Δρ<sub>max</sub>, Δρ<sub>min</sub> (e Å⁻³) | 0.26, −0.24 |

Computer programs: X-AREA and X-RED (Stoe, 2009), SHELXT2018/2 (Stoe, 2015a), SHELXL2018/3 (Stoe, 2015b), XP (Stoe, 2008), WinGX (Farrugia, 2012), publCIF (Westrip, 2010) and shelXle (Hübschle et al., 2011).

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Crystal structure of 9,9-diethyl-9H-fluorene-2,4,7-tricarbaldehyde

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Computing details
Data collection: X-AREA (Stoe, 2009); cell refinement: X-AREA (Stoe, 2009); data reduction: X-RED (Stoe, 2009); program(s) used to solve structure: SHELXT2018/2 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: XP (Sheldrick, 2008); software used to prepare material for publication: WinGX (Farrugia, 2012), publCIF (Westrip, 2010), and shelXle (Hübschle et al., 2011).

Crystal data
\[
\begin{align*}
C_{20}H_{18}O_3 & \\
M_r = 306.34 & \\
Monoclinic, P2_1/c & \\
a = 15.6595 (9) \, \text{Å} & \\
b = 13.1466 (14) \, \text{Å} & \\
c = 7.6834 (15) \, \text{Å} & \\
\beta = 93.146 \, (9)^\circ & \\
V = 1579.4 (4) \, \text{Å}^3 & \\
Z = 4 & \end{align*}
\]

\[F(000) = 648\]
\[D_x = 1.288 \, \text{Mg} \, \text{m}^{-3}\]

Mo Kα radiation, \(\lambda = 0.71073 \, \text{Å}\)

Cell parameters from 6293 reflections
\[\theta = 2.9–28.3^\circ\]
\[\mu = 0.09 \, \text{mm}^{-1}\]
\[T = 150 \, \text{K}\]

Piece, colorless

0.38 × 0.30 × 0.15 mm

Data collection
Stoe IPDS 2T diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Plane graphite monochromator

Detector resolution: 6.67 pixels mm\(^{-1}\)
rotation method scans

13951 measured reflections
13951 independent reflections
8830 reflections with \(I > 2\sigma(I)\)
\[\theta_{\text{max}} = 25.0^\circ, \theta_{\text{min}} = 3.0^\circ\]

\(h = -17\rightarrow 18\)
\(k = -15\rightarrow 15\)
\(l = -9\rightarrow 9\)

Refinement
Refinement on \(F^2\)
Least-squares matrix: full

\[R[F^2 > 2\sigma(F^2)] = 0.047\]
\[wR(F^2) = 0.127\]
\[S = 0.93\]
13951 reflections
211 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
\[w = 1/\left[\sigma^2(F_c^2) + (0.0713P)^2\right]\]
where \(P = (F_c^2 + 2F_s^2)/3\)
\[(\Delta/\sigma)_{\text{max}} < 0.001\]

\(\Delta\rho_{\text{max}} = 0.26 \, \text{e} \, \text{Å}^{-3}\)
\(\Delta\rho_{\text{min}} = -0.24 \, \text{e} \, \text{Å}^{-3}\)
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.

Refinement. Refined as a two-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|     | x      | y      | z      | Uiso * / Ueq |
|-----|--------|--------|--------|--------------|
| O1  | 0.51535 (14) | 0.34892 (18) | 0.5435 (3) | 0.0532 (7)   |
| O2  | 0.15641 (16) | 0.18707 (17) | -0.0059 (3) | 0.0604 (7)   |
| O3  | 0.03712 (16) | 0.7414 (2)   | -0.2592 (4) | 0.0713 (8)   |
| C1  | 0.37790 (18) | 0.4293 (2)   | 0.3116 (3)  | 0.0322 (7)   |
| H1  | 0.414572    | 0.480263    | 0.361567    | 0.039*       |
| C2  | 0.39372 (18) | 0.3258 (2)   | 0.3466 (3)  | 0.0316 (7)   |
| C3  | 0.33905 (17) | 0.2531 (2)   | 0.2722 (4)  | 0.0330 (6)   |
| H3  | 0.350875    | 0.183387    | 0.295850    | 0.040*       |
| C4  | 0.26770 (17) | 0.2774 (2)   | 0.1647 (3)  | 0.0313 (7)   |
| C5  | 0.11308 (18) | 0.4025 (2)   | -0.0802 (4) | 0.0372 (7)   |
| H5  | 0.099564    | 0.332138    | -0.087467   | 0.045*       |
| C6  | 0.06274 (19) | 0.4738 (2)   | -0.1701 (4) | 0.0412 (8)   |
| H6  | 0.014947    | 0.451369    | -0.241394   | 0.049*       |
| C7  | 0.08030 (19) | 0.5775 (2)   | -0.1586 (4) | 0.0385 (7)   |
| C8  | 0.15063 (18) | 0.6120 (2)   | -0.0543 (4) | 0.0364 (7)   |
| C9  | 0.162721    | 0.682613    | -0.044365   | 0.044*       |
| C10 | 0.28194 (18) | 0.5627 (2)   | 0.1500 (4)  | 0.0313 (7)   |
| C11 | 0.30798 (17) | 0.4554 (2)   | 0.2032 (3)  | 0.0294 (6)   |
| C12 | 0.25144 (17) | 0.3818 (2)   | 0.1286 (3)  | 0.0291 (6)   |
| C13 | 0.18436 (17) | 0.4364 (2)   | 0.0215 (3)  | 0.0305 (6)   |
| C14 | 0.20206 (18) | 0.5414 (2)   | 0.0338 (3)  | 0.0311 (7)   |
| C15 | 0.46610 (18) | 0.2932 (2)   | 0.4635 (4)  | 0.0379 (7)   |
| C16 | 0.474848    | 0.222039    | 0.477297    | 0.045*       |
| C17 | 0.2180 (2)  | 0.1882 (2)   | 0.0975 (4)  | 0.0436 (8)   |
| C18 | 0.236754    | 0.123771    | 0.140831    | 0.052*       |
| C19 | 0.0245 (2)  | 0.6512 (3)   | -0.2560 (5) | 0.0535 (9)   |
| C20 | -0.024467   | 0.625546    | -0.320103   | 0.064*       |
| H17A| 0.315855    | 0.636730    | 0.382697    | 0.044*       |
| H17B| 0.245393    | 0.697499    | 0.266210    | 0.044*       |
| C18 | 0.1931 (2)  | 0.5885 (2)   | 0.4212 (4)  | 0.0466 (8)   |
| H18A| 0.190690    | 0.630388    | 0.526375    | 0.070*       |
| H18B| 0.206083    | 0.518019    | 0.454380    | 0.070*       |
| H18C| 0.137719    | 0.591187    | 0.355334    | 0.070*       |
| C19 | 0.35203 (19) | 0.6155 (2)   | 0.0494 (4)  | 0.0388 (7)   |
| H19A| 0.331460    | 0.684240    | 0.015221    | 0.047*       |
| H19B| 0.403150    | 0.624283    | 0.129659    | 0.047*       |
| C20 | 0.3791 (2)  | 0.5611 (3)   | -0.1127 (4) | 0.0516 (9)   |

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### Atomic displacement parameters (Å²)

|   | $U_{11}$   | $U_{22}$   | $U_{33}$   | $U_{12}$   | $U_{13}$   | $U_{23}$   |
|---|------------|------------|------------|------------|------------|------------|
| O1| 0.0435 (13)| 0.0551 (15)| 0.0591 (14)| −0.0035 (12)| −0.0151 (13)| 0.0044 (13) |
| O2| 0.0656 (15)| 0.0508 (15)| 0.0633 (15)| −0.0157 (12)| −0.0094 (14)| −0.0051 (12)|
| O3| 0.0680 (16)| 0.0551 (16)| 0.0880 (18)| 0.0021 (15) | −0.0219 (16)| 0.0182 (15) |
| C1| 0.0309 (15)| 0.0348 (16)| 0.0311 (13)| −0.0035 (13)| 0.0026 (13) | −0.0008 (12)|
| C2| 0.0302 (15)| 0.0353 (16)| 0.0296 (15)| 0.0015 (13) | 0.0045 (13) | 0.0014 (12) |
| C3| 0.0389 (15)| 0.0300 (15)| 0.0308 (14)| 0.0026 (14) | 0.0072 (14) | 0.0007 (12) |
| C4| 0.0349 (15)| 0.0303 (16)| 0.0292 (14)| −0.0029 (13)| 0.0071 (14) | −0.0032 (12)|
| C5| 0.0341 (16)| 0.0363 (16)| 0.0409 (16)| −0.0056 (14)| 0.0000 (14) | −0.0041 (14)|
| C6| 0.0320 (17)| 0.049 (2)  | 0.0421 (17)| −0.0048 (15)| −0.0037 (15)| −0.0012 (14)|
| C7| 0.0332 (16)| 0.0450 (19)| 0.0371 (15)| 0.0006 (14) | −0.0003 (14)| 0.0057 (14) |
| C8| 0.0360 (16)| 0.0350 (16)| 0.0381 (16)| −0.0038 (14)| 0.0003 (14) | 0.0044 (13) |
| C9| 0.0330 (15)| 0.0263 (14)| 0.0344 (14)| −0.0022 (12)| −0.0008 (13)| 0.0009 (12) |
| C10| 0.0303 (15)| 0.0301 (15)| 0.0280 (13)| −0.0010 (13)| 0.0034 (13) | −0.0004 (12)|
| C11| 0.0314 (15)| 0.0289 (15)| 0.0274 (13)| −0.0020 (13)| 0.0042 (12) | −0.0018 (12)|
| C12| 0.0287 (15)| 0.0321 (15)| 0.0309 (14)| −0.0024 (12)| 0.0036 (13) | −0.0014 (13)|
| C13| 0.0316 (15)| 0.0350 (16)| 0.0381 (16)| −0.0030 (13)| 0.0001 (13) | −0.0002 (13)|
| C14| 0.0355 (16)| 0.0414 (17)| 0.0371 (17)| 0.0051 (15) | 0.0056 (15) | 0.0057 (15) |
| C15| 0.050 (2)  | 0.0422 (19)| 0.0389 (17)| −0.0085 (16)| 0.0045 (17) | −0.0019 (15)|
| C16| 0.044 (2)  | 0.055 (2)  | 0.060 (2)  | −0.0005 (18)| −0.0105 (18)| 0.0115 (19) |
| C17| 0.0403 (17)| 0.0308 (15)| 0.0378 (15)| 0.0010 (14) | −0.0054 (14)| −0.0035 (13)|
| C18| 0.0519 (19)| 0.0454 (19)| 0.0427 (17)| 0.0051 (16) | 0.0043 (16) | −0.0022 (15)|
| C19| 0.0378 (16)| 0.0349 (16)| 0.0430 (16)| −0.0097 (13)| −0.0046 (15)| 0.0071 (14) |
| C20| 0.0473 (19)| 0.060 (2)  | 0.0478 (18)| −0.0153 (18)| 0.0095 (16) | 0.0028 (17) |

### Geometric parameters (Å, °)

|   | O1—C14  | 1.207 (3) | C9—C13  | 1.523 (4) |
|---|---------|-----------|---------|-----------|
| O2—C15  | 1.216 (3) | C9—C19  | 1.542 (4) |
| O3—C16  | 1.203 (4) | C9—C17  | 1.542 (4) |
| C1—C10  | 1.382 (4) | C10—C11 | 1.411 (4) |
| C1—C2   | 1.406 (4) | C11—C12 | 1.483 (4) |
| C1—H1   | 0.9500   | C12—C13 | 1.410 (4) |
| C2—C3   | 1.386 (4) | C14—H14 | 0.9500   |
| C2—C14  | 1.471 (4) | C15—H15 | 0.9500   |
| C3—C4   | 1.390 (4) | C16—H16 | 0.9500   |
| C3—H3   | 0.9500   | C17—C18 | 1.522 (5) |
| C4—C11  | 1.421 (4) | C17—H17A| 0.9900   |
| C4—C15  | 1.484 (4) | C17—H17B| 0.9900   |
| C5—C6   | 1.384 (4) | C18—H18A| 0.9800   |
| C5—C12  | 1.400 (4) | C18—H18B| 0.9800   |
| C5—H5   | 0.9500   | C18—H18C| 0.9800   |
| Bond          | Length (Å) | Bond          | Length (Å) |
|--------------|------------|--------------|------------|
| C6—C7        | 1.393 (4)  | C19—C20      | 1.517 (5)  |
| C6—H6        | 0.9500     | C19—H19A     | 0.9900     |
| C7—C8        | 1.401 (4)  | C19—H19B     | 0.9900     |
| C7—C16       | 1.479 (4)  | C20—H20A     | 0.9800     |
| C8—C13       | 1.381 (4)  | C20—H20B     | 0.9800     |
| C8—H8        | 0.9500     | C20—H20C     | 0.9800     |
| C9—C10       | 1.518 (4)  |              |            |
| C10—C1—C2    | 118.8 (2)  | C13—C12—C11 | 107.8 (2)  |
| C10—C1—H1    | 120.6      | C8—C13—C12  | 121.2 (2)  |
| C2—C1—H1     | 120.6      | C8—C13—C9   | 127.0 (2)  |
| C3—C2—C1     | 119.4 (2)  | C12—C13—C9  | 111.8 (2)  |
| C3—C2—C14    | 119.2 (3)  | O1—C14—C2   | 125.7 (3)  |
| C1—C2—C14    | 121.4 (2)  | O1—C14—H14  | 117.2      |
| C2—C3—C4     | 123.0 (3)  | C2—C14—H14  | 117.2      |
| C2—C3—H3     | 118.5      | O2—C15—C4   | 128.2 (3)  |
| C4—C3—H3     | 118.5      | O2—C15—H15  | 115.9      |
| C3—C4—C11    | 117.9 (2)  | C4—C15—H15  | 115.9      |
| C3—C4—C15    | 114.4 (3)  | O3—C16—C7   | 124.2 (3)  |
| C11—C4—C15   | 127.7 (2)  | O3—C16—H16  | 117.9      |
| C6—C5—C12    | 118.5 (3)  | C7—C16—H16  | 117.9      |
| C6—C5—H5     | 120.7      | C18—C17—C9  | 115.5 (2)  |
| C12—C5—H5    | 120.7      | C18—C17—H17A| 108.4      |
| C5—C6—C7     | 121.8 (2)  | C9—C17—H17A | 108.4      |
| C5—C6—H6     | 119.1      | C18—C17—H17B| 108.4      |
| C7—C6—H6     | 119.1      | C9—C17—H17B | 108.4      |
| C6—C7—C8     | 119.9 (3)  | H17A—C17—H17B| 107.5     |
| C6—C7—C16    | 120.0 (3)  | C17—C18—H18A| 109.5      |
| C8—C7—C16    | 120.1 (3)  | C17—C18—H18B| 109.5      |
| C13—C8—C7    | 118.8 (3)  | H18A—C18—H18B| 109.5    |
| C13—C8—H8    | 120.6      | C17—C18—H18C| 109.5      |
| C7—C8—H8     | 120.6      | H18A—C18—H18C| 109.5    |
| C10—C9—C13   | 100.8 (2)  | H18B—C18—H18C| 109.5   |
| C10—C9—C19   | 111.4 (2)  | C20—C19—C9  | 116.0 (2)  |
| C13—C9—C19   | 111.9 (2)  | C20—C19—H19A| 108.3      |
| C10—C9—C17   | 112.0 (2)  | C9—C19—H19A | 108.3      |
| C13—C9—C17   | 112.1 (2)  | C20—C19—H19B| 108.3      |
| C19—C9—C17   | 108.6 (2)  | C9—C19—H19B | 108.3      |
| C1—C10—C11   | 122.2 (2)  | H19A—C19—H19B| 107.4   |
| C1—C10—C9    | 125.8 (2)  | C19—C20—H20A| 109.5      |
| C11—C10—C9   | 112.0 (2)  | C19—C20—H20B| 109.5      |
| C10—C11—C4   | 118.8 (2)  | H20A—C20—H20B| 109.5  |
| C10—C11—C12  | 107.6 (2)  | C19—C20—H20C| 109.5      |
| C4—C11—C12   | 133.6 (2)  | H20A—C20—H20C| 109.5   |
| C5—C12—C13   | 119.8 (2)  | H20B—C20—H20C| 109.5   |
| C5—C12—C11   | 132.4 (2)  |              |            |
| C10—C1—C2—C3| −0.1 (4)   |              |            |
| C10—C11—C12—C5| 180.0 (3)|              |            |
C10—C1—C2—C14 −178.8 (3) C4—C11—C12—C5 0.6 (6)
C1—C2—C3—C4 −0.7 (4) C10—C11—C12—C13 0.1 (3)
C14—C2—C3—C4 178.0 (3) C4—C11—C12—C13 −179.3 (3)
C2—C3—C4—C15 0.8 (4) C7—C8—C13—C12 −0.6 (5)
C2—C3—C4—C11 179.6 (3) C7—C8—C13—C9 178.7 (3)
C12—C5—C6—C7 −1.3 (5) C5—C12—C13—C8 −0.6 (4)
C5—C6—C7—C16 −179.6 (3) C4—C11—C12—C13 −179.3 (3)
C6—C7—C8—C13 0.9 (5) C11—C12—C13—C8 179.3 (3)
C6—C7—C8—C13 −0.1 (3) C5—C12—C13—C9 −180.0 (3)
C1—C10—C11—C4 −0.1 (4) C3—C4—C15—O2 −175.4 (3)
C9—C10—C11—C12 179.4 (3) C6—C7—C16—O3 −176.7 (4)
C9—C10—C11—C10 179.7 (3) C8—C7—C16—O3 3.5 (6)
C3—C4—C11—C10 −0.1 (4) C13—C9—C17—C18 54.8 (3)
C15—C4—C11—C10 −178.6 (3) C19—C9—C17—C18 57.6 (3)
C3—C4—C11—C12 0.7 (5) C13—C9—C17—C18 −55.3 (3)
C6—C5—C12—C13 1.5 (4) C17—C9—C17—C18 −179.6 (2)
C6—C5—C12—C11 −178.3 (3)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|------|--------|
| C1—H1···O1i | 0.95 | 2.59 | 3.512 (4) | 165 |
| C5—H5···O2 | 0.95 | 2.18 | 2.961 (4) | 138 |
| C5—H5···O3ii | 0.95 | 2.67 | 3.350 (4) | 129 |
| C16—H16···O2iii | 0.95 | 2.53 | 3.321 (4) | 141 |
| C17—H17A···O1i | 0.99 | 2.68 | 3.611 (4) | 157 |

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) −x, y−1/2, −z−1/2; (iii) −x, y+1/2, −z−1/2.