Crystal structure and Hirshfeld surface analysis of (3aSR,6RS,6aSR,7RS,11bSR,11cRS)-2,2-dibenzyl-2,3,6a,11c-tetrahydro-1H,6H,7H-3a,6:7,11b-di-epoxydibenzo[de,h]isoquinolin-2-ium trifluoromethanesulfonate

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In the cation of the title salt, C30H28NO2+·CF3O3S−, the four tetrahydrofuran rings adopt envelope conformations. In the crystal, pairs of cations are linked by dimeric C—H ··· O hydrogen bonds, forming two R22(6) ring motifs parallel to the (001) plane. The cations and anions are connected by further C—H ··· O hydrogen bonds, forming a three-dimensional network structure. Hirshfeld surface analysis indicates that the most important contributions to the crystal packing are from H···H (47.6%), C···H···H/C···C (20.6%), O···H···O (18.0%) and F···H···F (9.9%) interactions.

1. Chemical context

Intramolecular Diels–Alder reactions (Krishna et al., 2021) are powerful tools in the arsenal of modern organic chemistry. In particular, the IMDAF cycloaddition (the intramolecular furan Diels–Alder reaction) based on renewable starting materials (e.g. furfural, furfuryl alcohol, etc.) is frequently used in natural product synthesis and in many other practically useful applications (for reviews on the topic, see: Zubkov et al., 2005; Takao et al., 2005; Juhl et al., 2009; Padwa et al., 2013; Parvatkar et al., 2014). Cascade sequences including two or more successive [4 + 2] cycloaddition steps to furan moieties are less known because of difficulties in accessing the starting materials. However, these tandem strategies open up an easy way for the construction of multifunctional naphthalene derivatives, which can be obtained in one synthetic step. At the same time, it becomes possible to create four or more chiral centres in one synthetic stage with exceptional chemo-, regio- and diastereoselectivity (Criado et al., 2010, 2013; Zubkov et al., 2012, 2014). Previously, it was shown that the [4 + 2] cycloaddition of bis-furyldienes with derivatives of maleic acid, esters of acetylene dicarboxylic acid or hexafluoro-2-butyne proceeds in all cases with excellent diastereo- and chemoselectivity, and leads, depending on the temperature, to annelated diepoxynaphthalenes of the ‘domino’ or ‘pincer’ type (Borisova et al., 2018a,b).

In order to expand the limits of the applicability of the IMDAF strategy, during the current study we tested dehydrobenzene generated in situ in the role of a dienophile. It
was found that N-benzylidifurfurylamine under the action of dehydrobenzene forms a multicomponent mixture, from which three major components (1–3) were isolated using column chromatography (Fig. 1). Compound 1, the most interesting from a chemical point of view, was chosen for structural analysis using diffraction data.

In general, non-covalent interactions such as hydrogen bonding, ionic and π-interactions play critical roles in synthesis and catalysis, as well as in the organization of the supramolecular structures as a result of their significant contribution to the self-assembly process (Gurbanov et al., 2020a,b; Khalilov et al., 2018a,b; Ma et al., 2017a,b, 2020, 2021; Mahmudov et al., 2012, 2020; Mizar et al., 2012). Thus, the interplay of non-covalent interactions has an impact on solubility (Shixaliyev et al., 2019) and other functional properties of 1.

2. Structural commentary
In the cation \((\text{C}_{30}\text{H}_{28}\text{NO}_{2})^+\) of the title salt 1 (Fig. 2), the tetrahydrofuran rings (O12/C7/C6A/C11/C11B, O12/C7/C7A/C11A/C11B, O13/C3A/C4/C5/C6 and O13/C3A/C11/C6A/C6d) adopt envelope conformations with the following puckering parameters (Cremer & Pople, 1975): \(Q(2) = 0.5504 (8) \text{ Å}, \varphi(2) = 181.08 (9)^\circ, Q(2) = 0.5474 (9) \text{ Å}, \varphi(2) = 0.24 (10)^\circ, Q(2) = 0.5260 (9) \text{ Å}, \varphi(2) = 1.91 (11)^\circ\) and \(Q(2) = 0.5610 (9) \text{ Å}, \varphi(2) = 175.78 (9)^\circ\), respectively. The molecular conformation of the cation is stabilized by weak intramolecular C21–H21B...O12 and C21–H21B...O13 contacts (Table 1). The piperidine ring (N2/C1/C11B/C11C/C3A/C3) in the cation exhibits a chair conformation [puckering parameters are \(Q_T = 0.4871 (9) \text{ Å}, \theta = 175.22 (11)^\circ\) and \(\varphi = 281.2 (12)^\circ\)]. The benzene ring (C7A/C8–C11/C11A) fused with the central tetrahydrofuran ring makes dihedral angles of 53.43 (5) and 58.64 (5)^\circ, respectively, with the C22–C27 and C32–C37 phenyl rings of the benzyl groups attached to the N atom. These phenyl rings make a dihedral angle of 73.81 (5)^\circ with each other.

3. Supramolecular features and Hirshfeld surface analysis
In the crystal, pairs of cations are linked by dimeric C6–H6A...O12^ii and C7–H7A...O13^iii hydrogen bonds [symmetry code: (ii) \(-x + 1, -y + 1, -z + 1\); (iii) \(-x + 1, -y + 1, -z + 1\)] forming two \(R_2^2(6)\) ring motifs (Bernstein et al., 1995) parallel to the (001) plane (Table 1; Fig. 3). Furthermore, the cations and anions

![Figure 1](image1.png)

**Figure 1**
Synthesis scheme of the title compound 1 and its by-products.

![Figure 2](image2.png)

**Figure 2**
The asymmetric unit of the title salt 1 with displacement ellipsoids for the non-hydrogen atoms drawn at the 30% probability level.
are connected by intermolecular C1—H1\(\cdot\)O1, C6—H6\(\cdot\)O12, C6A—H6AA\(\cdot\)O3, C7—H7A\(\cdot\)O13, C31—H31\(\cdot\)O2 and C9—H9A\(\cdot\)Cg10 hydrogen bonds, forming a three-dimensional network (Table 1; Figs. 4, 5 and 6).

The intermolecular interactions (Table 2) were quantified and displayed using CrystalExplorer17.5 (Turner et al., 2017). Fig. 7 shows the Hirshfeld surface plotted over \(d_{norm}\) in the range −0.2715 to 1.3713 a.u. where C—H\(\cdot\)O interactions are shown as red dots. The overall two-dimensional fingerprint plot, as well as those delineated into the main contacts, are shown in Fig. 8. The H\(\cdot\)H (Fig. 8b) interactions constitute the primary factor in the crystal packing, with C\(\cdot\)H/H\(\cdot\)C (Fig. 8c), O\(\cdot\)H/H\(\cdot\)O (Fig. 8d) and F\(\cdot\)H/H\(\cdot\)F (Fig. 8e) interactions constituting the next stronger contributions. Numerical values of these interactions together with other percentage contributions of weaker interactions are compiled in Table 3.
4. Database survey

A search of the Cambridge Structural Database (CSD version 5.40, update of September 2019; Groom et al., 2016) for structures having an epoxysindole moiety gave ten hits that closely resemble the title salt, viz. IQOTOA (Mertsalov et al., 2021a), OMUTAU (Mertsalov et al., 2021b), OMEMAX (Mertsalov et al., 2021c), IMUBIE (Mertsalov et al., 2021a), AGONUH (Temel et al., 2013), TIJMIK (Demircan et al., 2013), YAXCIL (Temel et al., 2012), UPAQEI (Koşar et al., 2011), ERIVIL (Temel et al., 2011) and MIGTIG (Koşar et al., 2007).

IQOTOA, OMUTAU and OMEMAX each crystallize with two molecules in the asymmetric unit. In the crystal, molecule pairs generate centrosymmetric rings with $R_2^2(8)$ motifs linked by C–H–O hydrogen bonds. These pairs of molecules form a tetrameric supramolecular motif, leading to molecular layers parallel to the (100) plane by C–H–π and C–Br–π interactions. Interlayer van der Waals and interhalogen interactions stabilize the molecular packing. In the crystal of OMUTAU, strong intermolecular O–H–O hydrogen bonds and weak intermolecular C–H–O contacts link the molecules, forming a three-dimensional network. In addition, weak π–π stacking interactions between the pyrrolidine rings of the nine-membered groups of molecules are observed. In the crystal of OMEMAX, molecules are linked by weak C–

| Contact   | Distance | Symmetry operation |
|-----------|----------|--------------------|
| H7A···O13 | 2.41     | 1 − x, 1 − y, 1 − z |
| H4A···H11A| 2.34     | −1 + x, 1/2 − y, −1/2 + z |
| H31A···O2 | 2.33     | 2 − x, 1 − y, 1 − z |
| H37A···O3 | 2.65     | −1 + x, 1/2 + y, 1/2 − z |
| H6A4···O3 | 2.50     | 1 − x, 1 − y, 1 − z |
| H9A···C8  | 2.01     | −1/2 + x, −1/2 + y, 1/2 − z |
| H1B···H24A| 2.60     | 1/2 + x, 1/2 + y, 1/2 + z |
| H10A···H26A| 2.31    | x, y, 1 + z |
| C24···F1  | 3.202    | x, y, z |
| C25···H36A| 3.50     | −1/2 − x, 1/2 + y, 1/2 − z |
| H5A···H23A| 2.53     | −1 + x, y, z |
| H10A···O2 | 2.91     | −1/2 − x, 1/2 + y, 1/2 − z |

Table 3
Percentage contributions of interatomic contacts to the Hirshfeld surface of the title salt 1.

| Contact   | Percentage contribution |
|-----------|------------------------|
| H···H     | 47.6                   |
| C···H/H···C| 20.6                   |
| O···H/H···O| 18.0                   |
| F···H/H···F| 9.9                    |
| F···C/C···F| 2.2                    |
| C···C     | 1.0                    |
| O···C/C···O| 0.4                    |
| F···O/O···F| 0.1                    |

H···O hydrogen bonds, forming sheets lying parallel to the (002) plane. These sheets are connected only by weak van der Waals interactions. In the crystal of IMUBIE, the molecules

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Figure 7
Hirshfeld surface of the title molecule 1 mapped over $d_{norm}$.

Figure 8
Fingerprint plots showing (a) all intermolecular interactions and delineated into (b) H···H, (c) C···H/H···C, (d) O···H/H···O and (e) F···H/H···F contacts.
are linked into dimers by pairs of C—H···O hydrogen bonds, thus generating $R_2^2(18)$ rings. The crystal packing is dominated by H···H, Br···H, H···π and Br···π interactions. In the crystal structures of IQOTOA, OMUTAU, OMEMAX, AGONUH, TJMIK, YAXCIL, UPAQEI and ERIVIL, the molecules are predominantly linked by C—H···O hydrogen bonds describing different hydrogen-bonding pattern connectivities. In the crystal of AGONUH, the molecules are connected into zigzag chains running along the $b$-axis direction. In TJMIK, two types of C—H···O hydrogen bond motifs are found, viz. $R_2^2(20)$ and $R_2^2(26)$ rings, with adjacent rings running parallel to the $ac$ plane. Additionally, C—H···O hydrogen bonds form a C(6) chain, linking the molecules along the $b$-axis direction. In the crystal of ERIVIL, molecules are connected into $R_2^1(8)$ and $R_2^1(14)$ rings along the $b$ axis. In MIGTIG, the molecules are linked only by weak van der Waals interactions.

5. Synthesis and crystallization

(3aSR,6aSR,6bSR,7bRS,11bSR,11cRS)-2,2-Dibenzyl-2,3,6a,11c-tetrahydro-1H,6H,7H-3a,6,7,11b-diepoxydibenzo[de, h]isoquinolin-2-i um trifluoromethanesulfonate (1)

Cesium fluoride (CsF) (1.7 g, 0.011 mol) was added to benzylbis(furan-2-ylmethyl)amine (0.0022 mol) dissolved in dry CH$_2$CN (20 ml). Then an equivalent of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1) was added to the solution under an argon atmosphere. The least mobile fraction represented the target residue (yellow oil) turned out to be a multicomponent mixture. It was separated using column chromatography on silica gel. The least mobile fraction was filtered off through a thin layer of SiO$_2$, and the resulting product, 1, was obtained by slow crystallization from ethyl acetate.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 4. All C-bound H atoms were placed at calculated positions using a riding model, with C—H = 0.95–1.00 Å, and with $U_{	ext{iso}}$(H) = 1.2$U_{	ext{eq}}$(C). Five reflections (011, 101, 020, 0101 and 110), which were obscured by the beam stop as well as eight outliers (021, 111, 11 T 1 12, 218, 610, 143, 572 and 581) were omitted during the final cycle of refinement.

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The authors’ contributions are as follows. Conceptualization, MA and SM; synthesis, ZA and GZM; X-ray analysis, GZM; writing (review and editing of the manuscript), ZA and MA; supervision, MA and SM.

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Crystal structure and Hirshfeld surface analysis of
(3aSR,6RS,6aSR,7RS,11bSR,11cRS)-2,2-dibenzyl-2,3,6a,11c-tetrahydro-1H,6H,7H-3a,6:7,11b-diepoxydibenzo[de,h]isoquinolin-2-ium trifluoromethanesulfonate

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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: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: PLATON (Spek, 2020).

(3aSR,6RS,6aSR,7RS,11bSR,11cRS)-2,2-Dibenzyl-2,3,6a,11c-tetrahydro-1H,6H,7H-3a,6:7,11b-diepoxydibenzo[de,h]isoquinolin-2-ium trifluoromethanesulfonate

Crystal data
C\textsubscript{30}H\textsubscript{28}NO\textsubscript{2}\textsuperscript{+}·CF\textsubscript{3}O\textsubscript{3}S\textsuperscript{−}

\( M_r = 583.60 \)

Monoclinic, \( P2_1/n \)

\( a = 11.1507(9) \AA \)

\( b = 18.4653(15) \AA \)

\( c = 12.8519(10) \AA \)

\( \beta = 91.786(4)^\circ \)

\( V = 2644.9(4) \AA^3 \)

\( Z = 4 \)

\( \mu = 0.19 \text{ mm}^{-1} \)

\( D_x = 1.466 \text{ Mg m}^{-3} \)

\( \rho(000) = 1216 \)

\( \theta = 2.7–34.6^\circ \)

\( \lambda = 0.71073 \text{ Å} \)

\( T = 100 \text{ K} \)

Fragment, colourless

\( 0.40 \times 0.32 \times 0.16 \text{ mm} \)

Data collection
Bruker KAPPA APEXII area-detector

\( \varphi \) and \( \omega \) scans

Absorption correction: multi-scan

\( \text{(SADABS; (Bruker, 2013))} \)

\( T_{\text{min}} = 0.924, \ T_{\text{max}} = 0.971 \)

101039 measured reflections

11684 independent reflections

9164 reflections with \( I > 2\sigma(I) \)

\( R_{\text{int}} = 0.038 \)

\( \theta_{\text{max}} = 35.1^\circ, \ \theta_{\text{min}} = 3.3^\circ \)

\( h = -18\rightarrow18 \)

\( k = -29\rightarrow29 \)

\( l = -20\rightarrow20 \)

Refinement
Refinement on \( F^2 \)

\( R[F^2 > 2\sigma(F^2)] = 0.039 \)

\( wR(F^2) = 0.109 \)

\( S = 1.04 \)

11684 reflections

370 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

\[ w = \frac{1}{0.027(F_o^2 + 0.8665P)} \]
where \( P = (F_o^2 + 2F_c^2)/3 \)

\[ (\Delta \sigma)_{\max} = 0.001 \]
\[ \Delta \rho_{\max} = 0.56 \text{ e Å}^{-3} \]
\[ \Delta \rho_{\min} = -0.32 \text{ e Å}^{-3} \]

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 (\( \text{Å}^2 \))**
Atomic displacement parameters ($\overline{A^2}$)

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|-----|------------|------------|------------|------------|------------|------------|
| C1  | 0.0115 (3) | 0.0134 (3) | 0.0132 (3) | −0.0015 (3) | −0.0003 (3) | 0.0007 (3) |
| C3  | 0.0111 (3) | 0.0128 (3) | 0.0155 (3) | 0.0004 (3)  | −0.0014 (3) | 0.0016 (3) |
| C3A | 0.0103 (3) | 0.0116 (3) | 0.0153 (3) | 0.0002 (3)  | −0.0011 (3) | 0.0009 (3) |
| C4  | 0.0117 (3) | 0.0177 (4) | 0.0183 (4) | 0.0022 (3)  | −0.0029 (3) | 0.0004 (3) |
| C5  | 0.0113 (3) | 0.0219 (4) | 0.0207 (4) | −0.0005 (3) | −0.0027 (3) | 0.0017 (3) |
| C6  | 0.0113 (3) | 0.0155 (4) | 0.0188 (4) | −0.0029 (3) | 0.0003 (3)  | −0.0024 (3) |
| C6A | 0.0110 (3) | 0.0125 (3) | 0.0175 (3) | −0.0014 (3) | 0.0014 (3)  | −0.0012 (3) |
| C7  | 0.0128 (3) | 0.0113 (3) | 0.0179 (4) | −0.0013 (3) | 0.0031 (3)  | −0.0003 (3) |
| C7A | 0.0130 (3) | 0.0129 (3) | 0.0170 (3) | 0.0009 (3)  | 0.0019 (3)  | 0.0011 (3) |
| C8  | 0.0176 (4) | 0.0152 (4) | 0.0194 (4) | 0.0019 (3)  | 0.0045 (3)  | 0.0039 (3) |
| C9  | 0.0194 (4) | 0.0204 (4) | 0.0168 (4) | 0.0063 (3)  | 0.0041 (3)  | 0.0038 (3) |

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Geometric parameters (Å, °)

| Bond  | Distance     | Bond  | Distance     |
|-------|--------------|-------|--------------|
| C1—C11B | 1.5014 (12) | C21—C22 | 1.5043 (12) |
| C1—N2 | 1.5132 (11)  | C21—N2 | 1.5421 (11)  |
| C1—H1A | 0.9900       | C21—H21A | 0.9900       |
| C1—C1B | 0.9900       | C21—H21B | 0.9900       |
| C3—C3A | 1.5077 (12)  | C22—C27 | 1.3956 (13)  |
| C3—N2 | 1.5198 (11)  | C22—C23 | 1.3967 (13)  |
| C3—H3A | 0.9900       | C23—C24 | 1.3909 (13)  |
| C3—H3B | 0.9900       | C23—H23A | 0.9500       |
| C3A—O13 | 1.4427 (10) | C24—C25 | 1.3870 (15)  |
| C3A—C4 | 1.5231 (12)  | C24—H24A | 0.9500       |
| C3A—C11C | 1.5514 (12) | C25—C26 | 1.3869 (17)  |
| C4—C5 | 1.3339 (13)  | C25—H25A | 0.9500       |
| C4—H4A | 0.9500       | C26—C27 | 1.3925 (15)  |
| C5—C6 | 1.5253 (14)  | C26—H26A | 0.9500       |
| C5—H5A | 0.9500       | C27—H27A | 0.9500       |

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| Bond               | Distance (Å) | Bond               | Distance (Å) | Bond               | Distance (Å) |
|--------------------|--------------|--------------------|--------------|--------------------|--------------|
| C6—O13             | 1.4515 (11)  | C31—C32            | 1.5074 (12)  | C31—H31A          | 0.9900       |
| C6—C6A             | 1.5543 (13)  | C31—N2             | 1.5365 (11)  | C31—H31B          | 0.9900       |
| C6—H6A             | 1.0000       | C32—C37            | 1.3952 (13)  | C32—C33           | 1.4007 (13)  |
| C6A—C11C           | 1.5500 (12)  | C32—C37            | 1.3952 (13)  | C33—C34           | 1.3921 (14)  |
| C6A—C7             | 1.5544 (13)  | C33—C34            | 1.3921 (14)  | C33—H33A          | 0.9500       |
| C6A—H6AA           | 1.0000       | C34—C35            | 1.3869 (17)  | C34—H34A          | 0.9500       |
| C7—O12             | 1.4560 (11)  | C35—C36            | 1.3897 (16)  | C35—H35A          | 0.9500       |
| C7—C7A             | 1.5214 (13)  | C36—C37            | 1.3955 (14)  | C36—H36A          | 0.9500       |
| C7—H7A             | 1.0000       | C37—H37A           | 0.9500       | C37—H37A          | 0.9500       |
| C7A—C8             | 1.3787 (13)  | C12—F1             | 1.3318 (14)  | C12—F2            | 1.3333 (14)  |
| C7A—C11A           | 1.4014 (12)  | C12—F2             | 1.3333 (14)  | C12—F3            | 1.3357 (13)  |
| C8—C9              | 1.4029 (14)  | C12—S1             | 1.8271 (12)  | C12—S1            | 1.4404 (9)   |
| C8—H8A             | 0.9500       | O1—S1              | 1.4404 (9)   | O1—S1             | 1.4476 (8)   |
| C9—C10             | 1.3876 (15)  | O2—S1              | 1.4476 (8)   | O2—S1             | 1.4387 (8)   |
| C9—H9A             | 0.9500       | C27—C22—C23        | 118.90 (9)   | C27—C22—C23       | 118.90 (9)   |
| C10—C11            | 1.4037 (13)  | C22—C21—N2         | 117.07 (7)   | C22—C21—N2        | 117.07 (7)   |
| C10—H10A           | 0.9500       | C22—C21—H21A       | 108.0        | C22—C21—H21A      | 108.0        |
| C11—C11A           | 1.3800 (12)  | N2—C21—H21A        | 108.0        | N2—C21—H21A       | 108.0        |
| C11—H11A           | 0.9500       | C22—C21—H21B       | 108.0        | C22—C21—H21B      | 108.0        |
| C11A—C11B          | 1.5125 (12)  | C23—C22—C23        | 112.51 (8)   | C23—C22—C23       | 112.51 (8)   |
| C11B—O12           | 1.4494 (10)  | C24—C23—C22        | 119.12 (8)   | C24—C23—C22       | 119.12 (8)   |
| C11B—C11C          | 1.5369 (12)  | O13—C22—C23        | 119.6        | O13—C22—C23       | 119.6        |
| C11C—H11B          | 1.0000       | C25—C24—C23        | 119.6        | C25—C24—C23       | 119.6        |
|                    |              | C26—C25—C24        | 119.99 (9)   | C26—C25—C24       | 119.99 (9)   |
|                    |              | C27—C26—C25        | 120.0        | C27—C26—C25       | 120.0        |
|                    |              | C25—C25—C26        | 120.0        | C25—C25—C26       | 120.0        |
|                    |              | C24—C24—C26        | 120.0        | C24—C24—C26       | 120.0        |
|                    |              | C23—C23—C26        | 120.0        | C23—C23—C26       | 120.0        |
|                    |              | C22—C22—C26        | 120.0        | C22—C22—C26       | 120.0        |
|                    |              | C21—C21—C26        | 120.0        | C21—C21—C26       | 120.0        |
| Bond          | Distance (Å) | Angle (°) |
|--------------|-------------|-----------|
| O13—C6—C5   | 100.79 (7)  | 119.9     |
| O13—C6—C6A  | 102.46 (7)  | 119.9     |
| C5—C6—C6A   | 106.05 (7)  | 115.24 (7)|
| O13—C6—H6A  | 115.3       | 108.5     |
| C5—C6—H6A   | 115.3       | 108.5     |
| C6A—C6—H6A  | 115.3       | 108.5     |
| C11C—C6A—C6 | 100.00 (7)  | 108.5     |
| C11C—C6A—C7 | 100.40 (7)  | 107.5     |
| C6—C6A—C7   | 117.10 (7)  | 119.13 (8)|
| C11C—C6A—C6 | 112.6       | 120.24 (8)|
| C6—C6A—H6A  | 112.6       | 120.30 (8)|
| C6A—C6—H6A  | 112.6       | 120.40 (9)|
| O12—C7—C7A  | 99.81 (7)   | 119.8     |
| O12—C7—C6A  | 102.95 (7)  | 119.8     |
| C7A—C7—C6A  | 107.06 (7)  | 120.19 (9)|
| O12—C7—H7A  | 115.1       | 119.9     |
| C6A—C7—H7A  | 115.1       | 119.9     |
| C6A—C7—H7A  | 115.1       | 119.9     |
| C7A—C8—C9   | 117.80 (9)  | 120.1     |
| C7A—C8—H8A  | 121.1       | 120.1     |
| C9—C8—H8A   | 121.1       | 120.11 (9)|
| C10—C9—C8   | 121.38 (9)  | 119.9     |
| C10—C9—H9A  | 119.3       | 119.9     |
| C8—C9—H9A   | 119.3       | 119.9     |
| C9—C10—C11  | 120.66 (9)  | 110.23 (6)|
| C9—C10—H10A | 119.7       | 108.19 (6)|
| C11—C10—H10A| 119.7       | 107.41 (6)|
| C11A—C11—C10| 117.51 (9)  | 111.80 (6)|
| C11A—C11—H11A| 121.2      | 108.33 (7)|
| C10—C11—H11A| 121.2       | 96.31 (6) |
| C11—C11A—C7A| 121.86 (8)  | 95.89 (6) |
| C11—C11A—C11B| 133.76 (8) | 108.40 (11)|
| C7A—C11A—C11B| 104.27 (7)| 107.55 (10)|
| O12—C11B—C1 | 115.03 (7)  | 107.45 (9)|
| O12—C11B—C11A| 100.71 (6) | 110.65 (8)|
| C1—C11B—C11A| 117.03 (7)  | 111.39 (8)|
| O12—C11B—C11C| 102.84 (6) | 111.23 (8)|
| C1—C11B—C11C| 113.06 (7)  | 115.08 (5)|
| C11A—C11B—C11C| 106.53 (7)| 115.39 (5)|
| C11B—C11C—C6A| 102.54 (7) | 114.31 (6)|
| C11B—C11C—C3A| 111.64 (7) | 103.67 (5)|
| C6A—C11C—C3A| 102.16 (6)  | 103.51 (6)|
| C11B—C11C—H11B| 113.2     | 102.48 (5)|
| N2—C3—C3A—O13| 72.16 (9)  | O13—C3A—C11C—C6A| 31.68 (8)|
| Bond  | Distance (Å)  | Bond  | Distance (Å)  |
|-------|---------------|-------|---------------|
| N2—C3 | 1.6947 (7)    | C3—C3A | 0.69 (8)      |
| N2—C3—C3A—C4 | 45.73 (10) | C3A—C4—C5 | 34.74 (9) |
| O13—C3A—C4—C5 | 7.191 (9)  | C6C—C3A—C1 | 1.85 (10) |
| C3—C3A—C4—C5 | 45.73 (10)  | C4—C3A—C1 | 75.15 (9)  |
| O13—C6—C6A—C11C | 38.02 (8) | C6A—C6—C7—O12 | 72.18 (9) |
| N2—C1—C11B—C11A | 50.16 (9) | C11B—C11C—C11B | 49.72 (9) |
| N2—C1—C11B—C11C | 74.93 (8) | C1—C11B—O12 | 65.09 (9) |
| C1—C11B—C11C | 158.40 (7) | C11B—C11C—C11B | 24.55 (14) |
| C1—C11B—O12 | 65.09 (9)  | C7A—C11A—C11B | 158.40 (7) |
| C1—C11B—C11C | 158.40 (7) | C11A—C11B—C1 | 158.40 (7) |
| C1—C11B—O12 | 149.99 (10) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—C11C | 158.40 (7) | C11C—C11B—O12 | 103.03 (11) |
| C1—C11B—O12 | 149.99 (10) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—C11C | 158.40 (7) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—O12 | 149.99 (10) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—C11C | 158.40 (7) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—O12 | 149.99 (10) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—C11C | 158.40 (7) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—O12 | 149.99 (10) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—C11C | 158.40 (7) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—O12 | 149.99 (10) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—C11C | 158.40 (7) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—O12 | 149.99 (10) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—C11C | 158.40 (7) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—O12 | 149.99 (10) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—C11C | 158.40 (7) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—O12 | 149.99 (10) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—C11C | 158.40 (7) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—O12 | 149.99 (10) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—C11C | 158.40 (7) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—O12 | 149.99 (10) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—C11C | 158.40 (7) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—O12 | 149.99 (10) | C7A—C11A—C11B | 24.55 (14) |
| C1—C11B—C11C | 158.40 (7) | C7A—C11A—C11B | 24.55 (14) |
|          | D—H···A                | D—H | H···A | D···A    | D—H···A |
|----------|------------------------|------|-------|----------|----------|
| C1—H1A···O1i | 0.99 2.49 3.4043 (13) | 154  |       |          |          |
| C6—H6A···O12ii | 1.00 2.52 3.3040 (11) | 135  |       |          |          |
| C6A—H6AA···O3ii | 1.00 2.50 3.4407 (12) | 157  |       |          |          |
| C7—H7A···O13ii | 1.00 2.41 3.2563 (11) | 142  |       |          |          |
| C21—H21B···O12 | 0.99 2.33 2.9151 (11) | 117  |       |          |          |
| C21—H21B···O13 | 0.99 2.35 3.0974 (11) | 132  |       |          |          |
| C31—H31A···O2i | 0.99 2.33 3.2751 (13) | 159  |       |          |          |
| C9—H9A···Cg10iii | 0.95 2.71 3.2958 (11) | 121  |       |          |          |

Symmetry codes: (i) −x+2, −y+1, −z+1; (ii) −x+1, −y+1, −z+1; (iii) x−1/2, −y+3/2, z+1/2.