Synthesis and crystal structure of ebastinium hydrogen fumarate

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The structure of ebastinium hydrogen fumarate [systematic name: 1-[4-(4-tert-butylphenyl)-4-oxobutyl]-4-(diphenylmethoxy)piperidin-1-ium (E)-3-carboxy-1-hydroxyprop-2-en-1-olate], C32H40NO2⁺·C4H3O4⁻, a 1:1 salt formed in the reaction between ebastine and fumaric acid is presented. All examined crystals were found to be twinned by pseudo-merohedry. The structure is extensively disordered, with over half (20 out of 35) its non-hydrogen atoms modelled as lying over two sets of sites. In the crystal, cation–anion pairs are linked by a strong N—H ·· O hydrogen bond [N···O = 2.697 (11) Å]. These units interact via weaker C—H···O and C—H···π contacts to form layers lying parallel to the bc plane. The hydrogen fumarate anions are linked by a very short O—H···O hydrogen bond [O···O = 2.5402 (17) Å], augmented by weak C—H···O contacts into pairs of R2(6) ring motifs to form chains that extend parallel to the b-axis direction. Comparisons to similar crystal structures are presented.

1. Chemical context

The second-generation antihistamine ebastine, C32H39NO2, systematic name 4-(benzylhydroxy)-1-[4-[4-(tert-butyl)phenyl]-4-oxobutyl]piperidine, is an H1 receptor antagonist that acts by blocking H1 receptors via its carboxylic acid metabolite, carebastine (Yamaguchi et al., 1994). It is prescribed mainly for allergic rhinitis and chronic idiopathic urticaria (hives) (Van Cauwenberge et al., 2004). A review of its pharmacological properties and clinical efficacy in the treatment of allergic disorders has been reported by Wiseman & Faulds (1996). Formulations of ebastine and its salts with various counter-anions have been the subject of numerous patents (see, for example, Bobee et al., 1995; Roma-Millan et al., 2011; Bilgic, 2013). In spite of this, only the crystal structures of the neutral free-base molecule (Cheng et al., 2005; Sharma et al., 2015) and the salt ebastinium 3,5-dinitrobenzoate (Shaibah et al., 2017) have been reported to date. By contrast, fumarates (di-anion fumarate and mono-anion hydrogen fumarate) are common counter-anions in compounds of pharmacological importance; examples include oppraminium fumarate (Siddegowda et al., 2011), cinnarizininium fumarate (Kavitha et al., 2013) (technically, both hydrogen fumarates), and the recently reported structure of bis(4-acetoxy-N,N-dimethyltryptammonium)fumarate, a new crystalline form of psilacetin (Chadeayne et al., 2019). As part of our studies in this area, we now report the synthesis and crystal structure of the title 1:1 salt ebastinium hydrogen fumarate, C32H40NO2⁺·C4H3O4⁻, (I), formed in the reaction between ebastine and fumaric acid.
2. Structural commentary

All examined samples of I were twinned by pseudo-merohedry, as is common for monoclinic crystals with β close to 90° (see, for example, Parkin, 2021). Further details on how this was handled are given in section 6 (Crystal handling, data collection and structure refinement). The asymmetric unit of I (Fig. 1) consists of a single ebastinium cation–hydrogen fumarate anion pair. The cation is extensively disordered, with over half (20 out of 35) its non-H atoms modelled as occupying two sets of sites, with refined occupancy factors of 0.729 (4) and 0.271 (4), as shown in Fig. 2. Unless stated otherwise, the numerical details in the following description apply to the major conformation.

The ebastinium cation is protonated at N1 (Fig. 1), which in turn forms a strong N–H···O hydrogen bond to the carboxylate O4 atom of the hydrogen fumarate anion [N1···O4 = 2.697 (11) Å, Table 1]. The piperidinium ring of the cation is in the expected chair conformation, with the 4-t-butylphenyl-4-oxobutyl substituent equatorial at N1 and the diphenylethoxymethoxy group about the C4—O1 and C1—O1 bonds (Fig. 2), the torsion angles C1—O1—C4—C5 and C4—O1—C33—O4, respectively, for the major component compared to 85.8 (11) and 68.67 (11)°, respectively, for the minor component. The dihedral angle between the phenyl rings is 73.41 (18)° in the major component [c.f. 73.3 (6)°, minor]. Additional details concerning the disorder are given in section 6 (Crystal handling, data collection and structure refinement).

The hydrogen fumarate anion deviates substantially from planarity, as indicated by the dihedral angle between its carboxylate and carboxylic acid groups of 23.51 (14)°. As expected, the C—O bond lengths in the deprotonated carboxylate group [1.2638 (18) and 1.2503 (18) Å for C33—O3 and C33—O4, respectively] are the same within the accuracy of measurement. The deprotonated carboxylate and carboxylic acid groups of 23.51 (14)°.

Table 1

| D−H···A | D−H | H···A | D···A | D−H···A |
|--------|-----|------|------|--------|
| N1−H1N···O4 | 0.95 | 1.75 | 2.697 (11) | 175 |
| N1'−H1N'···O4 | 1.00 | 1.78 | 2.77 (3) | 169 |
| O5−H5O···O3' | 1.04 (2) | 1.50 (2) | 2.5402 (17) | 171 (2) |
| C7−H7A···O2'' | 0.99 | 2.37 | 3.330 (2) | 164 |
| C8−H8B···O6'' | 0.99 | 2.53 | 3.325 (2) | 137 |
| C34−H34···O5' | 0.95 | 2.62 | 3.208 (2) | 121 |
| C35−H35···O3' | 0.95 | 2.49 | 3.1450 (19) | 127 |
| C31−H31···Cg1'v | 0.95 | 2.72 | 3.534 (6) | 145 |
| C25−H25···Cg1'v | 0.95 | 2.70 | 3.532 (4) | 146 |
| C23−H23···Cg2'' | 0.95 | 2.75 | 3.624 (4) | 154 |

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

Figure 1

An ellipsoid plot (50% probability) of I. The N−H···O hydrogen bond is shown as a dashed line. The minor component of disorder is omitted to enhance clarity.

Figure 2

A ball-and-stick plot showing the superposition of major (solid bonds) and minor (open bonds) in ebastinium hydrogen fumarate, I. Hydrogen atoms (except for piperidinium NH) are omitted to enhance clarity.

free-base ebastine (Cheng et al., 2005; Sharma et al., 2015). The phenyl-4-oxobutyl fragment is largely planar (r.m.s. deviation = 0.0814 Å for atoms C7–C16 and O2): the main deviation [0.1879 (13) Å] is at atom C7, as seen in the C7–C8–C9–C10 torsion angle of −168.02 (14)°. The major and minor disorder conformations arise as a result of superposition of components that differ primarily by rotation of the diphenylethoxymethoxy group about the C4—O1 and C1—O1 bonds (Fig. 2), the torsion angles C1—O1—C4—C5 and C4—O1—C33—O4, respectively, for the major disorder component compared to 85.8 (11) and 68.67 (11)°, respectively, for the minor component. The dihedral angle between the phenyl rings is 73.41 (18)° in the major component [c.f. 73.3 (6)°, minor]. Additional details concerning the disorder are given in section 6 (Crystal handling, data collection and structure refinement).

The hydrogen fumarate anion deviates substantially from planarity, as indicated by the dihedral angle between its carboxylate and carboxylic acid groups of 23.51 (14)°. As expected, the C—O bond lengths in the deprotonated carboxylate group [1.2638 (18) and 1.2503 (18) Å for C33—O3 and C33—O4, respectively] are the same within the accuracy of measurement.
limitations of the spherical-atom scattering-factor approximation (see, for example, Dawson, 1964), while those of the carboxylic acid group [1.3197 (19) and 1.211 (2) Å for C36—O5 and C36—O6, respectively] are significantly different. Indeed, throughout the whole structure there are no unusual bond lengths or angles in either species.

3. Supramolecular features

For the sake of clarity, the following description is restricted to the major component of disorder except where stated otherwise. The packing in I features only two types of conventional hydrogen bonds; the strong N1—H1N⋯O4 [N⋯O = 2.697 (11) Å, Table 1] link and a very short [2.5402 (17) Å] O5—H5O⋯O3ii hydrogen bond between hydrogen fumarate anions (vide infra). Much weaker C—H⋯O hydrogen bonds connect the ebastinium cations along the b-axis direction (C7—H7A⋯O2i), ebastinium and hydrogen fumarate ions via the c-glide (C8—H8B⋯O6ii) and hydrogen fumarate anions into chains parallel to the b-axis direction (C34—H34⋯O5i and C35—H35⋯O3iii). The symmetry operations are those defined in the footnote to Table 1. Since these weaker interactions do not involve disordered atoms, the above description applies equally well to both major and minor components.

There are no aromatic C—C stacking interactions, but there are C—H⋯π close contacts between the phenyl rings of the disordered diphenylmethoxy group, which are also summarized in Table 1.

The main structural motif in the extended structure of I is the cation–anion pair (Fig. 1). In the crystal, chemically distinct groups are segregated such that the 4-t-butylphenyl groups interdigitate with c-glide-related copies of themselves (Fig. 3) and the diphenylmethoxy groups interact via the aforementioned C—H⋯π contacts (Fig. 4), forming layers that extend parallel to the bc plane and stack along the a-axis direction. The hydrogen fumarate anions form chains that propagate along the b-axis direction by virtue of the O5—H5O⋯O3ii, C34—H34⋯O5i and C35—H35⋯O3iii
hydrogen bonds (Fig. 5), which form pairs of $R^2_2(6)$ ring motifs (Etter et al., 1990).

A rigorous Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) is complicated by the extensive disorder in I, but fingerprint plots generated for the major disorder component using CrystalExplorer (Spackman et al., 2021) (Fig. 6) provide a reasonable summary of atom–atom contacts (Fig. 6). The most prevalent are H···H contacts (55%), followed by C···H/ H···C (23.5%) and O···H/H···O (21.3%), with all other contacts being negligible.

4. Database survey

A search of the Cambridge Structure Database (version 5.43 with updates as of June 2022; Groom et al., 2016) for the keywords ‘ebastine’ or ‘ebastinium’ revealed only two hits, CSD refcode QATJIF (Cheng et al., 2005) and the duplicate QATJIF01 (Sharma et al., 2015); both are structures of the free base, ebastine. An ebastinium salt with 3,5-dinitrobenzoate was not returned in this search, but is present as entry HECMIO (Shaibah et al., 2017). A search using the molecular fragment that extends from the ether oxygen atom through to and including the benzene ring (atoms O1/O2/N1/C2–C16 in this report) but including no other atoms, gave 38 unique structures (46 hits, eight of which were duplicates). Many of these were originally published in the pharmaceutical chemistry literature, highlighting the medicinal importance of the central core of the ebastine molecule. In contrast, a search for the keyword ‘fumarate’ gave 434 hits, covering a wide variety of structures with both the mono-anion and di-anion.

A detailed comparison of the ebastine structure (coordinates taken from QATJIF01) with the 3,5-dinitrobenzoate salt (HECMIO) was made by Shaibah et al. (2017). The free base (i.e., QATJIF and QATJIF01) is not disordered, but HECMIO has a relatively simple two-component disorder of the benzene ring of its 4-t-butylphenyl substituent. Of particular note (Shaibah et al., 2017) was the placement of the (C6H5)2CHO group relative to the piperidine/piperidinium ring, which is equatorial in ebastine, but axial in the ebastinium salt. The (C6H5)2CHO substituent in both disorder components of the hydrogen fumarate salt presented here is axial, as in HECMIO. The conformation of the C6H3O-4-t-butylphenyl fragment in I, however, is more similar to that in the neutral molecule (QATJIF and QATJIF01). An overlay of the major and minor disorder components of I with QATJIF01 and HECMIO highlights these conformational differences (Fig. 7).

5. Synthesis, crystallization and spectroscopic details

A sample of ebastine was obtained as a gift from R. L. Fine Chemicals, Bengaluru, India. Ebastine (100 mg, 0.21 mmol)
and fumaric acid (25 mg, 0.21 mmol) were dissolved in hot ethyl acetate and DMF and stirred over a heating magnetic stirrer for 30 minutes at 333 K. The resulting solution was allowed to cool slowly to room temperature with slow evaporation. Crystallization was carried out using several solvents (ethyl acetate/DMF, acetone, acetonitrile, and methyl ethyl ketone) via slow evaporation to give plate-shaped crystals in about a week (m.p. 468–470 K). All crystals allowed to cool slowly to room temperature with slow evaporation. Crystallization was carried out using several solvents (ethyl acetate/DMF, acetone, acetonitrile, and methyl ethyl ketone) via slow evaporation to give plate-shaped crystals in about a week (m.p. 468–470 K). All crystals observed were twinned by pseudo-merohedry, but those grown from acetonitrile were the largest and gave the best diffraction patterns [see section 6 (Crystal handling, data collection and structure refinement) for further details].

NMR spectra were recorded on an SA-AGILENT 400MHz NMR spectrometer: 1H NMR: DMSO-δ6 (400 MHz, δ ppm): 1.294 [s, 9H, C—(CH3)3]; 1.615–1.592 (d, 2H, J = 9.2 Hz, CH2); 1.871–1.818 (q, 4H, J = 6.8 Hz, piperidine); 2.400 (b, 2H, O==C—CH3); 2.576–2.541 (t, 2H, J = 7.2 Hz, piperidine); 2.870 (t, 2H, J = 7.2 Hz, CH2); 3.024–2.989 (d, 2H, J = 6.8 Hz, CH2); 3.423–3.406 (b, 1H, −CH), 5.63 (s, 1H, −CH); 6.557 (s, 2H, HC==CH); 7.250–7.207 (m, 2H, phenyl); 7.372–7.297 (m, 8H, phenyl); 7.533–7.512 (d, 2H, J = 8.4 Hz, phenyl); 7.891–7.870 (d, 2H, J = 8.4 Hz, phenyl); 11.6–14.2 (b, 1H, OH). 13C NMR: DMSO-δ6 (100 MHz, δ ppm): 20.04, 29.53, 30.78, 34.76, 35.25, 49.52, 55.93, 79.06, 125.39, 126.57, 127.13, 127.80, 128.25, 134.25, 134.57, 142.96, 156.03, 167.03, 198.80.

6. Crystal handling, data collection and structure refinement

Crystals from each of the aforementioned solvents [see section 5 (Synthesis, crystallization and spectroscopic details)] were thin plates that indexed to give essentially the same unit-cell dimensions. All specimens were pseudo-merohedral twins by virtue of the β angle being close to 90° and had roughly equal component volume fractions, as determined by the refined BASF parameter in SHELXL (Sheldrick, 2015b) for the twin operation corresponding to 180° rotation about the c-axis. A small number of the crystals grown from acetonitrile were somewhat thicker than most specimens, such that it was possible to cut along the twin plane, thereby separating individuals. Data collected from such a separated thin slice gave better refinement statistics than any of the uncut crystals. Nevertheless, the twin model was retained for the final refinement because, in spite of the very low occupancy minor component fraction of 0.19 (2)%, its standard uncertainty is only about one tenth as large, and is therefore of statistical significance. Even with such a tiny residual minor individual fraction, refinement statistics were marginally better with TWIN/BASF (in SHELXL) included. For a concise description of the various types of twinning that commonly affect molecular crystals, particularly twinning by pseudo-merohedry and the attendant twin operations that constitute the twin law, see Parkin (2021).

In addition to the twinning, the structure is extensively disordered. This disorder consists of a rotation of the (C6H5)2CHO group of the cation followed by a relaxation into the available space, which in turn places the whole of the (C6H5)2CHO group in two distinct orientations [see section 2 (Structural commentary)]. This of necessity must also cause minor site splitting of the piperidinum ring, albeit not discernible in electron-density maps calculated to 0.77 Å

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**Table 2**  
**Experimental details.**

| Crystal data | Chemical formula | C12H12O3·C6H5O4− |
|--------------|-----------------|------------------|
| Temperature (K) | 90 | |
| No. of parameters | 578 | |
| No. of restraints | 445 | |
| Rfactor | 0.047 | |
| S | 0.047, 0.114, 1.03 |
| Reflections | 7224 | |
| No. of observations | 19511 | |
| No. of H-atoms | 73 | |
| H Atoms treatment | H atoms treated by a mixture of independent and constrained refinement |
| Δρmin | 0.52, −0.19 |

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**Computer programs:** APEX3 (Bruker, 2016), SHELXT (Sheldrick, 2015a), SHELXL2018 (Sheldrick, 2018), XP in SHELXTL (Sheldrick, 2008), SHELXTL (Sheldrick, 2008) and pubCIF (Westrip, 2010).

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**Figure 7**  
An overlay of the major and minor conformations of the ebastinium cation in 1 (this work) with ebastine (CSD: QAT1IF01) and ebastinium cation from the 3,5-dinitrobenzoate salt (CSD: HECMIO, major conformation only), from a least-squares fit of non-H atoms in the piperidine/piperidinium rings. The axial placement of the diphenylmethoxy group (at left) in the salts is clearly different from the equatorial placement of the free base (blue). For the sake of clarity, only the major disorder component of HECMIO is shown. Diagram generated using Mercury (Macrae et al., 2020).
resolution. The two largest difference map peaks are only about 0.5 and 0.4 electrons, but are in positions that suggest a third, much smaller, disorder component. Such an additional disorder component, however, was not modelled due to its necessarily minuscule occupancy fraction. To ensure satisfactory refinement for disordered atom sequences in the structure, a combination of restraints were employed. The SHELXL commands SAME and SADI were used to maintain the chemical integrity and similarity of the disordered groups, while RIGU and SIMU were used to ensure physically reasonable displacement parameters for closely proximate disordered atom pairs.

Crystal data, data collection and structure refinement details are summarized in Table 2. All non-disordered and major-component H atoms were found in difference-Fourier maps. Carbon-bound hydrogen atoms were subsequently included in the refinement using riding models, with constrained distances set to 0.95 Å ($R_2Csp^2H$), 0.98 Å ($RCH_3$), 0.99 Å ($R_2CH_2$) and 1.00 Å ($R_3CH$). The N—H hydrogen atom was included using a riding model that allowed the N—H distance to refine, while that of the minor component was constrained. The O—H hydrogen atom coordinates of the hydrogen fumarate anion were refined freely. $U_{iso}(H)$ parameters were set to values of either 1.2 $U_{eq}$ ($R_2CspH$, $R_2CH_2$, $R_2CH$, NH) or 1.5 $U_{eq}$ ($R_3CH$, OH) of the attached atom. The final structure was checked using validation tools in PLATON (Spek, 2020) and checkCIF.

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Supporting information

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Computing details
Data collection: APEX3 (Bruker, 2016); cell refinement: APEX3 (Bruker, 2016); data reduction: APEX3 (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2019/2 (Sheldrick, 2015b); molecular graphics: XP in SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL (Sheldrick, 2008) and publCIF (Westrip, 2010).

1-[4-(4-tert-Butylphenyl)-4-oxobutyl]-4-(diphenylmethoxy)piperidin-1-ium (E)-3-carboxy-1-hydroxyprop-2-en-1-olate

Crystal data

C_{32}H_{40}NO_{2}^+\cdotC_4H_3O_4^-  
F(000) = 1256
D_x = 1.232 Mg m^-3
Monoclinic, P2_1/c
Mo Kα radiation, λ = 0.71073 Å
a = 27.091 (3) Å
Cell parameters from 9606 reflections
b = 6.2408 (5) Å
θ = 2.3–27.3°
c = 18.685 (2) Å
μ = 0.08 mm^{-1}
β = 90.975 (3)°
T = 90 K
V = 3158.6 (6) Å^3
Plate, colourless
Z = 4
0.24 × 0.14 × 0.03 mm

Data collection

55813 measured reflections
Bruker D8 Venture dual source diffractometer
7224 independent reflections
Radiation source: microsource
5164 reflections with I > 2σ(I)
Detector resolution: 7.41 pixels mm^-1
θ_max = 27.5°, θ_min = 2.2°
φ and ω scans
h = −35→35
Absorption correction: multi-scan
k = −7→8
(SADABS; Krause et al., 2015)
l = −24→24

Refinement

Refinement on F^2
Primary atom site location: structure-invariant direct methods
Least-squares matrix: full
Primary atom site location: difference Fourier map
R[F^2 > 2σ(F^2)] = 0.047
Secondary atom site location: difference Fourier map
wR(F^2) = 0.114
Hydrogen site location: mixed
S = 1.03
H atoms treated by a mixture of independent and constrained refinement
7224 reflections
w = 1/[σ^2(F^2) + (0.0333P)^2 + 1.537P]
578 parameters
where P = (F^2 + 2F'^2)/3
445 restraints
$\Delta/\sigma_{\text{max}} = 0.001$
$\Delta \rho_{\text{max}} = 0.52 \, \text{e} \, \text{Å}^{-3}$
$\Delta \rho_{\text{min}} = -0.19 \, \text{e} \, \text{Å}^{-3}$

Extinction correction: SHELXL2019/2 (Sheldrick 2015b),
$F_c^\text{c}=kF_c[1+0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0017 (4)

Special details

Experimental. The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid-nitrogen based cryostat (Hope, 1994; Parkin & Hope, 1998). Diffraction data were collected with the crystal at 90K, which is standard practice in this laboratory for the majority of flash-cooled crystals.

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 2-component twin.

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

|   | x    | y    | z    | Ueq,*/Ueq, | Occ. (<1) |
|---|------|------|------|------------|-----------|
| C7 | 0.20849 (6) | 0.7170 (3) | -0.16752 (10) | 0.0296 (4) |
| H7A | 0.185362 | 0.615042 | -0.190991 | 0.036* |
| H7B | 0.208016 | 0.689703 | -0.115336 | 0.036* |
| C8 | 0.19117 (6) | 0.9435 (3) | -0.18209 (9) | 0.0274 (4) |
| H8A | 0.190854 | 0.969760 | -0.234348 | 0.033* |
| H8B | 0.214680 | 1.045616 | -0.159546 | 0.033* |
| C9 | 0.14002 (6) | 0.9833 (3) | -0.15337 (9) | 0.0276 (4) |
| H9A | 0.118220 | 0.862657 | -0.167570 | 0.033* |
| H9B | 0.141905 | 0.986853 | -0.100427 | 0.033* |
| C10 | 0.11752 (6) | 1.1900 (3) | -0.18015 (9) | 0.0271 (4) |
| C11 | 0.06723 (6) | 1.2518 (3) | -0.15588 (9) | 0.0261 (4) |
| C12 | 0.04494 (7) | 1.4361 (3) | -0.18329 (10) | 0.0337 (4) |
| H12 | 0.061969 | 1.520883 | -0.217124 | 0.040* |
| C13 | -0.00150 (7) | 1.4973 (3) | -0.16206 (10) | 0.0347 (4) |
| H13 | -0.015849 | 1.623305 | -0.181951 | 0.042* |
| C14 | -0.02801 (6) | 1.3794 (3) | -0.11218 (9) | 0.0279 (4) |
| C15 | -0.00537 (6) | 1.1957 (3) | -0.08535 (11) | 0.0347 (4) |
| H15 | -0.022282 | 1.111001 | -0.051361 | 0.042* |
| C16 | 0.04111 (6) | 1.1326 (3) | -0.1067 (1) | 0.0339 (4) |
| H16 | 0.055326 | 1.005624 | -0.087336 | 0.041* |
| C17 | -0.08065 (6) | 1.4408 (3) | -0.09209 (10) | 0.0296 (4) |
| C18 | -0.08751 (8) | 1.6832 (3) | -0.09150 (13) | 0.0486 (5) |
| H18A | -0.082349 | 1.740047 | -0.139684 | 0.073* |
| H18B | -0.063553 | 1.747785 | -0.058064 | 0.073* |
| H18C | -0.121055 | 1.717576 | -0.076368 | 0.073* |
| C19 | -0.11537 (7) | 1.3419 (3) | -0.14877 (11) | 0.0415 (5) |
| H19A | -0.107029 | 1.397234 | -0.196135 | 0.062* |
| H19B | -0.149580 | 1.379546 | -0.138061 | 0.062* |
| H19C | -0.111696 | 1.185656 | -0.148334 | 0.062* |
| Atom  | x     | y     | z     | Uiso  | Ueq  |
|-------|-------|-------|-------|-------|------|
| C20   | -0.09453 (7) | 1.3543 (3) | -0.01864 (10) | 0.0426 (5) |
| H20A  | -0.127537  | 1.405422  | -0.006443  | 0.064* |
| H20B  | -0.070520  | 1.404689  | 0.017402   | 0.064* |
| H20C  | -0.094425  | 1.197298  | -0.019745  | 0.064* |
| O2    | 0.13952 (4) | 1.30433 (19) | -0.22189 (7) | 0.0338 (3) |
| N1    | 0.2608 (3)  | 0.6772 (14) | -0.1950 (5)  | 0.0207 (10)  | 0.729 (4) |
| H1N   | 0.2646 (3)  | 0.758 (3)  | -0.2376 (12) | 0.025* |
| O1    | 0.36765 (7) | 0.3639 (4)  | -0.14095 (11) | 0.0329 (5)  |
| C1    | 0.40693 (8) | 0.4053 (5)  | -0.08943 (14) | 0.0318 (6) |
| H1    | 0.401014 | 0.548461 | -0.067124 | 0.038* |
| C2    | 0.2990 (2)  | 0.7535 (8)  | -0.1414 (4)  | 0.0299 (10)  |
| H1A   | 0.2946 (3)  | 0.782540  | -0.136773  | 0.040* |
| C3    | 0.34996 (19) | 0.7376 (6)  | -0.1732 (3)  | 0.0337 (9)  |
| H1B   | 0.352040 | 0.837638 | -0.214153 | 0.040* |
| C4    | 0.3623 (2)  | 0.5110 (6)  | -0.1987 (2)  | 0.0319 (10) |
| H4    | 0.393500 | 0.514544 | -0.226516 | 0.038* |
| C5    | 0.3207 (2)  | 0.4260 (11) | -0.2459 (3)  | 0.0288 (9)  |
| H5A   | 0.327102 | 0.273168 | -0.256541 | 0.035* |
| C6    | 0.2701 (3)  | 0.4459 (13) | -0.2127 (4)  | 0.0251 (10) |
| H6A   | 0.244433 | 0.393366 | -0.246661 | 0.030* |
| C6B   | 0.268802 | 0.358040 | -0.168659 | 0.030* |
| C21   | 0.45774 (19) | 0.4068 (10) | -0.1223 (3)  | 0.0292 (10) |
| C22   | 0.49210 (17) | 0.5609 (7)  | -0.1025 (2)  | 0.0336 (9)  |
| H22   | 0.483326 | 0.665914 | -0.068179 | 0.040* |
| C23   | 0.53888 (16) | 0.5668 (6)  | -0.1312 (2)  | 0.0350 (9)  |
| H23   | 0.561954 | 0.673858 | -0.116928 | 0.042* |
| C24   | 0.55123 (14) | 0.4129 (7)  | -0.18122 (19) | 0.0336 (9) |
| H24   | 0.583134 | 0.413880 | -0.201546 | 0.040* |
| C25   | 0.51727 (14) | 0.2575 (6)  | -0.20178 (19) | 0.0327 (8) |
| H25   | 0.526049 | 0.152763 | -0.236204 | 0.039* |
| C26   | 0.47069 (15) | 0.2537 (8)  | -0.1725 (3)  | 0.0306 (9)  |
| H26   | 0.447625 | 0.146595 | -0.186809 | 0.037* |
| C27   | 0.40034 (17) | 0.2352 (7)  | -0.0330 (2)  | 0.0351 (10) |
| C28   | 0.3544 (2)  | 0.2194 (9)  | 0.0017 (3)   | 0.0645 (16) |
| H28   | 0.328738 | 0.316813 | -0.010989 | 0.077* |
| C29   | 0.3459 (2)  | 0.0678 (7)  | 0.0528 (3)   | 0.0559 (15) |
| H29   | 0.315266 | 0.065145 | 0.076755 | 0.067* |
| C30   | 0.3820 (3)  | -0.0819 (13) | 0.0699 (5)   | 0.0431 (11) |
| H30   | 0.376530 | -0.184382 | 0.106513 | 0.052* |
| C31   | 0.4256 (2)  | -0.0818 (12) | 0.0338 (4)   | 0.0336 (12) |
| H31   | 0.450309 | -0.185406 | 0.044800 | 0.040* |
| C32   | 0.4336 (2)  | 0.0710 (8)  | -0.0191 (3)  | 0.0347 (12) |
| H32   | 0.462801 | 0.062460 | -0.046450 | 0.042* |
| N1'   | 0.2574 (7)  | 0.701 (4)   | -0.1860 (14) | 0.022 (2)  |
| H1N'  | 0.259455 | 0.772729 | -0.233740 | 0.026* |

*Estimated standard deviations are shown in parentheses.*
| Atoms | x     | y     | z     | x'    | y'    | z'    | x''   | y''   | z''   |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| C1′   | 0.3683 (2) | 0.4743 (11) | -0.1213 (3) | 0.0396 (15) | 0.271 (4) |
| C1′   | 0.4022 (2) | 0.2951 (12) | -0.1234 (4) | 0.0342 (15) | 0.271 (4) |
| H1′   | 0.391924 | 0.195831 | -0.162870 | 0.041* | 0.271 (4) |
| C2′   | 0.2961 (6) | 0.808 (2) | -0.1404 (12) | 0.030 (2) | 0.271 (4) |
| H2′1  | 0.298622 | 0.734598 | -0.093513 | 0.036* | 0.271 (4) |
| H2′2  | 0.286471 | 0.958811 | -0.131678 | 0.036* | 0.271 (4) |
| C3′   | 0.3462 (5) | 0.8030 (17) | -0.1763 (9) | 0.0317 (19) | 0.271 (4) |
| H3′1  | 0.344118 | 0.882281 | -0.222156 | 0.038* | 0.271 (4) |
| H3′2  | 0.371053 | 0.874878 | -0.145181 | 0.038* | 0.271 (4) |
| C4′   | 0.3621 (5) | 0.5761 (19) | -0.1902 (7) | 0.031 (2) | 0.271 (4) |
| C5′   | 0.393715 | 0.573293 | -0.217142 | 0.037* | 0.271 (4) |
| C6′   | 0.3218 (6) | 0.452 (3) | -0.2305 (9) | 0.032 (2) | 0.271 (4) |
| C7′   | 0.320513 | 0.501750 | -0.280718 | 0.039* | 0.271 (4) |
| C8′   | 0.330949 | 0.298078 | -0.230940 | 0.039* | 0.271 (4) |
| C9′   | 0.2710 (7) | 0.473 (4) | -0.1995 (12) | 0.024 (2) | 0.271 (4) |
| C10′  | 0.246455 | 0.408576 | -0.233113 | 0.029* | 0.271 (4) |
| C11′  | 0.269747 | 0.391902 | -0.154000 | 0.029* | 0.271 (4) |
| C12′  | 0.3942 (5) | 0.182 (2) | 0.0050 (9) | 0.067 (3) | 0.271 (4) |
| C13′  | 0.352840 | 0.422012 | 0.000961 | 0.080* | 0.271 (4) |
| C14′  | 0.3527 (6) | 0.152 (2) | 0.0638 (9) | 0.057 (3) | 0.271 (4) |
| C15′  | 0.329001 | 0.198259 | 0.097343 | 0.068* | 0.271 (4) |
| C16′  | 0.3762 (9) | 0.040 (4) | 0.0722 (14) | 0.044 (2) | 0.271 (4) |
| C17′  | 0.366492 | -0.136032 | 0.108873 | 0.053* | 0.271 (4) |
| C18′  | 0.4143 (6) | -0.096 (4) | 0.0273 (11) | 0.033 (3) | 0.271 (4) |
| C19′  | 0.432588 | -0.222590 | 0.037098 | 0.040* | 0.271 (4) |
| C20′  | 0.4264 (6) | 0.026 (2) | -0.0308 (9) | 0.037 (3) | 0.271 (4) |
| C21′  | 0.455824 | 0.001951 | -0.056525 | 0.044* | 0.271 (4) |
| C22′  | 0.4542 (5) | 0.368 (3) | -0.1355 (9) | 0.028 (2) | 0.271 (4) |
| C23′  | 0.4738 (4) | 0.546 (2) | -0.0998 (8) | 0.037 (3) | 0.271 (4) |
| C24′  | 0.453933 | 0.622240 | -0.067147 | 0.045* | 0.271 (4) |
| C25′  | 0.5210 (4) | 0.6117 (17) | -0.1108 (6) | 0.038 (2) | 0.271 (4) |
| C26′  | 0.533659 | 0.733207 | -0.085975 | 0.046* | 0.271 (4) |
| C27′  | 0.5502 (4) | 0.5038 (19) | -0.1574 (7) | 0.040 (3) | 0.271 (4) |
| C28′  | 0.582673 | 0.556029 | -0.164371 | 0.048* | 0.271 (4) |
| C29′  | 0.5355 (4) | 0.3231 (19) | -0.1952 (6) | 0.041 (3) | 0.271 (4) |
| C30′  | 0.556234 | 0.246170 | -0.226675 | 0.049* | 0.271 (4) |
| C31′  | 0.4869 (4) | 0.268 (2) | -0.1814 (7) | 0.033 (3) | 0.271 (4) |
| C32′  | 0.474349 | 0.146602 | -0.206531 | 0.040* | 0.271 (4) |
| C33′  | 0.25492 (5) | 0.8367 (2) | -0.36524 (8) | 0.0206 (3) | 
| C34′  | 0.24432 (6) | 0.9666 (2) | -0.43083 (8) | 0.0223 (3) | 
| C35′  | 0.244724 | 0.896818 | -0.476010 | 0.027* | 
| C36′  | 0.23444 (5) | 1.1729 (2) | -0.42912 (9) | 0.0214 (3) | 
| C37′  | 0.235790 | 1.247094 | -0.384736 | 0.026* | 
| C38′  | 0.22119 (6) | 1.2914 (3) | -0.49577 (9) | 0.0261 (4) | 
| C39′  | 0.24297 (4) | 0.64104 (17) | -0.36785 (6) | 0.0304 (3) | 
| C40′  | 0.27305 (4) | 0.92704 (17) | -0.31116 (6) | 0.0265 (3) | 
| C41′  | 0.21455 (5) | 1.49991 (18) | -0.48923 (7) | 0.0369 (3) | 

*Estimated standard deviations in parentheses.
### Atomic displacement parameters (Å²)

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|------|----------|----------|----------|----------|----------|----------|
| C7   | 0.0280 (8) | 0.0308 (9) | 0.0302 (10) | −0.0044 (7) | 0.0025 (7) | 0.0052 (8) |
| C8   | 0.0312 (8) | 0.0279 (9) | 0.0230 (9) | −0.0066 (7) | −0.0002 (7) | −0.0013 (7) |
| C9   | 0.0299 (8) | 0.0301 (9) | 0.0229 (9) | −0.0060 (7) | 0.0007 (7) | 0.0008 (7) |
| C10  | 0.0329 (8) | 0.0271 (9) | 0.0212 (9) | −0.0090 (7) | −0.0032 (7) | −0.0015 (7) |
| C11  | 0.0303 (8) | 0.0265 (9) | 0.0215 (9) | −0.0061 (7) | −0.0029 (7) | 0.0008 (7) |
| C12  | 0.0403 (10)| 0.0300 (9) | 0.0308 (10) | −0.0033 (8) | 0.0016 (8) | 0.0061 (8) |
| C13  | 0.0404 (10)| 0.0324 (10)| 0.0313 (11) | 0.0038 (8) | −0.0028 (8) | 0.0095 (8) |

Full dataset available in supporting information.
|          | x      | y      | z      | u    | v    | w    |
|----------|--------|--------|--------|------|------|------|
| C6'      | 0.033 (3) | 0.024 (4) | 0.016 (5) | 0.001 (3) | −0.009 (3) | 0.001 (3) |
| C21'     | 0.025 (3) | 0.053 (4) | 0.027 (4) | 0.004 (3) | −0.009 (3) | 0.015 (3) |
| C22'     | 0.048 (5) | 0.093 (5) | 0.060 (4) | 0.037 (4) | 0.017 (4) | 0.047 (4) |
| C23'     | 0.041 (4) | 0.077 (5) | 0.054 (4) | 0.030 (4) | 0.013 (4) | 0.030 (4) |
| C24'     | 0.030 (4) | 0.066 (5) | 0.036 (3) | 0.017 (3) | 0.006 (3) | 0.017 (4) |
| C25'     | 0.022 (5) | 0.044 (4) | 0.032 (4) | 0.005 (4) | −0.003 (4) | 0.006 (3) |
| C26'     | 0.034 (4) | 0.047 (5) | 0.030 (4) | 0.007 (4) | −0.003 (3) | 0.004 (4) |
| C27'     | 0.032 (3) | 0.033 (4) | 0.019 (4) | 0.006 (3) | −0.007 (3) | 0.004 (3) |
| C28'     | 0.030 (5) | 0.047 (5) | 0.035 (5) | 0.003 (4) | −0.004 (4) | 0.000 (4) |
| C29'     | 0.027 (5) | 0.044 (5) | 0.044 (6) | 0.001 (4) | −0.003 (4) | −0.013 (4) |
| C30'     | 0.037 (4) | 0.039 (7) | 0.043 (8) | 0.005 (4) | 0.001 (4) | 0.003 (4) |
| C31'     | 0.047 (6) | 0.042 (7) | 0.034 (6) | −0.004 (4) | 0.006 (5) | 0.002 (4) |
| C32'     | 0.039 (6) | 0.035 (4) | 0.026 (5) | 0.005 (4) | 0.004 (4) | 0.002 (3) |
| C33      | 0.0261 (7) | 0.0185 (8) | 0.0173 (8) | 0.0033 (6) | −0.0003 (6) | 0.0002 (6) |
| C34      | 0.0317 (8) | 0.0215 (8) | 0.0139 (8) | −0.0015 (6) | 0.0011 (6) | −0.0002 (6) |
| C35      | 0.0277 (8) | 0.0193 (8) | 0.0171 (8) | −0.0023 (6) | −0.0025 (6) | 0.0001 (6) |
| C36      | 0.0379 (9) | 0.0186 (8) | 0.0215 (9) | −0.0014 (7) | −0.0060 (7) | 0.0023 (7) |
| O3       | 0.0533 (7) | 0.0144 (6) | 0.0231 (7) | −0.0002 (5) | −0.0098 (5) | 0.0028 (5) |
| O4       | 0.0385 (6) | 0.0231 (6) | 0.0179 (6) | −0.0037 (5) | −0.0042 (5) | 0.0009 (5) |
| O5       | 0.0676 (9) | 0.0156 (6) | 0.0268 (7) | 0.0021 (6) | −0.0186 (6) | 0.0010 (5) |
| O6       | 0.0769 (9) | 0.0233 (6) | 0.0179 (7) | 0.0010 (6) | −0.0113 (6) | 0.0000 (5) |

**Geometric parameters (Å, °)**

|          |        | C25—H25 |        |        | C30—C31 |        |        | C31—C32 |        |
|----------|--------|---------|--------|--------|---------|--------|--------|---------|--------|
| C7—N1'   | 1.38 (2) |       | C25—H25 | 0.9500 |       |       |       |         |        |
| C7—C8    | 1.513 (2) |       | C26—H26 | 0.9500 |       |       |       |         |        |
| C7—N1    | 1.537 (8) |       | C27—C32 | 1.387 (6) |       |       |       |         |        |
| C7—H7A   | 0.9900 |       | C27—C28 | 1.417 (6) |       |       |       |         |        |
| C7—H7B   | 0.9900 |       | C28—C29 | 1.367 (6) |       |       |       |         |        |
| C8—C9    | 1.515 (2) |       | C28—H28 | 0.9500 |       |       |       |         |        |
| C8—H8A   | 0.9900 |       | C29—C30 | 1.385 (6) |       |       |       |         |        |
| C8—H8B   | 0.9900 |       | C29—H29 | 0.9500 |       |       |       |         |        |
| C9—C10   | 1.509 (2) |       | C30—C31 | 1.371 (7) |       |       |       |         |        |
| C9—H9A   | 0.9900 |       | C30—H30 | 0.9500 |       |       |       |         |        |
| C9—H9B   | 0.9900 |       | C31—C32 | 1.392 (6) |       |       |       |         |        |
| C10—O2   | 1.220 (2) |       | C31—H31 | 0.9500 |       |       |       |         |        |
| C10—C11  | 1.494 (2) |       | C32—H32 | 0.9500 |       |       |       |         |        |
| C11—C16  | 1.386 (2) |       | N1’—C6' | 1.494 (14) |       |       |       |         |        |
| C11—C12  | 1.392 (2) |       | N1’—C2' | 1.498 (14) |       |       |       |         |        |
| C12—C13  | 1.380 (2) |       | N1’—H1N' | 1.0000 |       |       |       |         |        |
| C12—H12  | 0.9500 |       | O1’—C4' | 1.443 (11) |       |       |       |         |        |
| C13—C14  | 1.396 (2) |       | O1’—C1' | 1.448 (9) |       |       |       |         |        |
| C13—H13  | 0.9500 |       | C1’—C27 | 1.500 (13) |       |       |       |         |        |
| C14—C15  | 1.389 (2) |       | C1’—C21 | 1.568 (12) |       |       |       |         |        |
| C14—C17  | 1.530 (2) |       | C1’—H1' | 1.0000 |       |       |       |         |        |
| C15—C16  | 1.385 (2) |       | C2’—C3 | 1.523 (13) |       |       |       |         |        |
| C15—H15  | 0.9500 |       | C2’—H2'1 | 0.9900 |       |       |       |         |        |
| C16—H16  | 0.9500 |       | C2’—H2'2 | 0.9900 |       |       |       |         |        |
| Bond          | Distance   | Bond          | Distance   |
|---------------|------------|---------------|------------|
| C17—C18       | 1.524 (3)  | C3′—C4′       | 1.504 (10) |
| C17—C20       | 1.528 (3)  | C3′—H3′1      | 0.9900     |
| C17—C19       | 1.534 (2)  | C3′—H3′2      | 0.9900     |
| C18—H18A      | 0.9800     | C4′—C5′       | 1.529 (12) |
| C18—H18B      | 0.9800     | C4′—H4′       | 1.0000     |
| C18—H18C      | 0.9800     | C5′—C6′       | 1.508 (14) |
| C19—H19A      | 0.9800     | C5′—H5′1      | 0.9900     |
| C19—H19B      | 0.9800     | C5′—H5′2      | 0.9900     |
| C19—H19C      | 0.9800     | C6′—H6′1      | 0.9900     |
| C20—H20A      | 0.9800     | C6′—H6′2      | 0.9900     |
| C20—H20B      | 0.9800     | C21′—C26′     | 1.350 (15) |
| C20—H20C      | 0.9800     | C21′—C22′     | 1.445 (16) |
| N1—C6         | 1.503 (5)  | C22′—C23′     | 1.392 (15) |
| N1—C2         | 1.505 (6)  | C22′—H22′     | 0.9500     |
| N1—H1N        | 0.95 (2)   | C23′—C24′     | 1.367 (15) |
| O1—C4         | 1.422 (4)  | C23′—H23′     | 0.9500     |
| O1—C1         | 1.446 (3)  | C24′—C25′     | 1.383 (16) |
| C1—C27        | 1.509 (5)  | C24′—H24′     | 0.9500     |
| C1—C21        | 1.517 (5)  | C25′—C26′     | 1.370 (16) |
| C1—H1         | 1.0000     | C25′—H25′     | 0.9500     |
| C2—C3         | 1.515 (5)  | C26′—C27′     | 0.9500     |
| C2—H2A        | 0.9900     | C27′—C28′     | 1.393 (14) |
| C2—H2B        | 0.9900     | C27′—C29′     | 1.394 (14) |
| C3—C4         | 1.531 (4)  | C28′—C29′     | 1.362 (10) |
| C3—H3A        | 0.9900     | C28′—H28′     | 0.9500     |
| C3—H3B        | 0.9900     | C29′—C30′     | 1.362 (11) |
| C4—C5         | 1.515 (5)  | C29′—H29′     | 0.9500     |
| C4—H4         | 1.0000     | C30′—C31′     | 1.385 (12) |
| C5—C6         | 1.519 (5)  | C30′—H30′     | 0.9500     |
| C5—H5A        | 0.9900     | C31′—C32′     | 1.391 (11) |
| C5—H5B        | 0.9900     | C31′—H31′     | 0.9500     |
| C6—H6A        | 0.9900     | C32′—H32′     | 0.9500     |
| C6—H6B        | 0.9900     | C33—O4        | 1.2503 (18) |
| C21—C22       | 1.384 (6)  | C33—O3        | 1.2638 (18) |
| C21—C26       | 1.390 (6)  | C33—C34       | 1.493 (2)  |
| C22—C23       | 1.385 (5)  | C34—C35       | 1.316 (2)  |
| C22—H22       | 0.9500     | C34—H34       | 0.9500     |
| C23—C24       | 1.385 (4)  | C35—C36       | 1.487 (2)  |
| C23—H23       | 0.9500     | C35—H35       | 0.9500     |
| C24—C25       | 1.387 (5)  | C36—O6        | 1.211 (2)  |
| C24—H24       | 0.9500     | C36—O5        | 1.3197 (19) |
| C25—C26       | 1.384 (4)  | O5—H5O        | 1.04 (2)   |
| N1—C7—C8      | 108.6 (11) | C25—C24—H24   | 119.8      |
| C8—C7—N1      | 112.1 (4)  | C26—C25—C24   | 120.5 (4)  |
| C8—C7—H7A     | 109.2      | C26—C25—H25   | 119.7      |
| N1—C7—H7A     | 109.2      | C24—C25—H25   | 119.7      |
| C8—C7—H7B     | 109.2      | C25—C26—C21   | 119.8 (4)  |
| Bond/Angle | Value 1 | Value 2 | Value 3 |
|-----------|---------|---------|---------|
| N1—C7—H7B | 109.2   |         |         |
| H7A—C7—H7B | 107.9   |         |         |
| C7—C8—C9  | 111.84 (13) |         |         |
| C7—C8—H8A | 109.2   |         |         |
| C9—C8—H8A | 109.2   |         |         |
| C7—C8—H8B | 109.2   |         |         |
| C9—C8—H8B | 109.2   |         |         |
| H8A—C8—H8B | 107.9   |         |         |
| C10—C9—C8  | 112.92 (14) |         |         |
| C10—C9—H9A | 109.0   |         |         |
| C8—C9—H9A  | 109.0   |         |         |
| C10—C9—H9B | 109.0   |         |         |
| C8—C9—H9B  | 109.0   |         |         |
| H9A—C9—H9B | 107.8   |         |         |
| O2—C10—C11 | 120.08 (16) |         |         |
| O2—C10—C9  | 120.87 (15) |         |         |
| C11—C10—C9 | 119.04 (14) |         |         |
| C11—C10—C12 | 117.66 (16) |         |         |
| C16—C11—C12 | 112.76 (15) |         |         |
| C16—C11—C10 | 119.57 (15) |         |         |
| C13—C12—C11 | 120.99 (17) |         |         |
| C13—C12—H12 | 119.5   |         |         |
| C11—C12—H12 | 119.5   |         |         |
| C12—C13—C14 | 121.86 (17) |         |         |
| C12—C13—H13 | 119.1   |         |         |
| C14—C13—H13 | 119.1   |         |         |
| C15—C14—C13 | 116.55 (16) |         |         |
| C15—C14—C17 | 121.72 (16) |         |         |
| C13—C14—C17 | 121.60 (15) |         |         |
| C16—C15—C14 | 121.91 (17) |         |         |
| C16—C15—H15 | 119.0   |         |         |
| C14—C15—H15 | 119.0   |         |         |
| C15—C16—C11 | 121.02 (16) |         |         |
| C15—C16—H16 | 119.5   |         |         |
| C11—C16—H16 | 119.5   |         |         |
| C18—C17—C20 | 108.19 (17) |         |         |
| C18—C17—C14 | 111.40 (15) |         |         |
| C20—C17—C14 | 112.13 (14) |         |         |
| C18—C17—C19 | 109.32 (16) |         |         |
| C20—C17—C19 | 108.70 (16) |         |         |
| C14—C17—C19 | 107.04 (15) |         |         |
| C17—C18—H18A | 109.5   |         |         |
| C17—C18—H18B | 109.5   |         |         |
| H18A—C18—H18B | 109.5   |         |         |
| C17—C18—H18C | 109.5   |         |         |
| H18A—C18—H18C | 109.5   |         |         |
| H18B—C18—H18C | 109.5   |         |         |
| C17—C19—H19A | 109.5   |         |         |
| C10—C9—C8  | 112.92 (14) |         |         |
| C10—C9—H9A  | 109.0   |         |         |
| C8—C9—H9A  | 109.0   |         |         |
| C10—C9—H9B | 109.0   |         |         |
| C8—C9—H9B  | 109.0   |         |         |
| C13—C12—C11 | 120.99 (17) |         |         |
| C13—C12—H12 | 119.5   |         |         |
| C11—C12—H12 | 119.5   |         |         |
| C12—C13—C14 | 121.86 (17) |         |         |
| C12—C13—H13 | 119.1   |         |         |
| C14—C13—H13 | 119.1   |         |         |
| C15—C14—C13 | 116.55 (16) |         |         |
| C15—C14—C17 | 121.72 (16) |         |         |
| C13—C14—C17 | 121.60 (15) |         |         |
| C16—C15—C14 | 121.91 (17) |         |         |
| C16—C15—H15 | 119.0   |         |         |
| C14—C15—H15 | 119.0   |         |         |
| C15—C16—C11 | 121.02 (16) |         |         |
| C15—C16—H16 | 119.5   |         |         |
| C11—C16—H16 | 119.5   |         |         |
| C18—C17—C20 | 108.19 (17) |         |         |
| C18—C17—C14 | 111.40 (15) |         |         |
| C20—C17—C14 | 112.13 (14) |         |         |
| C18—C17—C19 | 109.32 (16) |         |         |
| C20—C17—C19 | 108.70 (16) |         |         |
| C14—C17—C19 | 107.04 (15) |         |         |
| C17—C18—H18A | 109.5   |         |         |
| C17—C18—H18B | 109.5   |         |         |
| H18A—C18—H18B | 109.5   |         |         |
| C17—C18—H18C | 109.5   |         |         |
| H18A—C18—H18C | 109.5   |         |         |
| H18B—C18—H18C | 109.5   |         |         |
| C17—C19—H19A | 109.5   |         |         |
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|----------------------|-----------|----------------------|-----------|
| C17—C19—H19B        | 109.5     | O1'—C4'—H4'         | 110.8     |
| H19A—C19—H19B       | 109.5     | C3'—C4'—H4'         | 110.8     |
| C17—C19—H19C        | 109.5     | C5'—C4'—H4'         | 110.8     |
| H19B—C19—H19C       | 109.5     | C6'—C5'—C4'         | 114.7 (11) |
| C17—C20—H20A        | 109.5     | C6'—C5'—H5'1        | 108.6     |
| C17—C20—H20B        | 109.5     | C4'—C5'—H5'1        | 108.6     |
| H20A—C20—H20B       | 109.5     | C6'—C5'—H5'2        | 108.6     |
| C17—C20—H20C        | 109.5     | H5'1—C5'—H5'2       | 107.6     |
| H20A—C20—H20C       | 109.5     | N1'—C6'—C5'         | 112.1 (15) |
| H20B—C20—H20C       | 109.5     | N1'—C6'—H6'1        | 109.2     |
| C6—N1—C2            | 109.6 (5) | C5'—C6'—H6'1        | 109.2     |
| C6—N1—C7            | 112.8 (6) | N1'—C6'—H6'2        | 109.2     |
| C2—N1—C7            | 110.8 (5) | C5'—C6'—H6'2        | 109.2     |
| C6—N1—H1N           | 107.8     | H6'1—C6'—H6'2       | 107.9     |
| C2—N1—H1N           | 107.8     | C26'—C21'—C22'      | 119.0 (13) |
| C7—N1—H1N           | 107.8     | C26'—C21'—C1'       | 117.0 (11) |
| C4—O1—C1            | 117.0 (3) | C22'—C21'—C1'       | 121.5 (11) |
| O1—C1—C27           | 104.2 (2) | C23'—C22'—C21'      | 117.2 (14) |
| O1—C1—C21           | 113.2 (3) | C23'—C22'—H22'      | 121.4     |
| C27—C1—C21          | 114.0 (3) | C21'—C22'—H22'      | 121.4     |
| O1—C1—H1            | 108.4     | C24'—C23'—C22'      | 118.6 (14) |
| C27—C1—H1           | 108.4     | C24'—C23'—H23'      | 120.7     |
| C21—C1—H1           | 108.4     | C22'—C23'—H23'      | 120.7     |
| N1—C2—C3            | 109.8 (5) | C23'—C24'—C25'      | 120.1 (17) |
| N1—C2—H2A           | 109.7     | C23'—C24'—H24'      | 120.0     |
| C3—C2—H2A           | 109.7     | C25'—C24'—H24'      | 120.0     |
| N1—C2—H2B           | 109.7     | C26'—C25'—C24'      | 122.2 (17) |
| C3—C2—H2B           | 109.7     | C26'—C25'—H25'      | 118.9     |
| H2A—C2—H2B          | 108.2     | C24'—C25'—H25'      | 118.9     |
| C2—C3—C4            | 112.8 (3) | C21'—C26'—C25'      | 116.3 (15) |
| C2—C3—H3A           | 109.0     | C21'—C26'—H26'      | 121.8     |
| C4—C3—H3A           | 109.0     | C25'—C26'—H26'      | 121.8     |
| C2—C3—H3B           | 109.0     | C28'—C27'—C32'      | 114.2 (11) |
| C4—C3—H3B           | 109.0     | C28'—C27'—C1'       | 121.5 (11) |
| H3A—C3—H3B          | 107.8     | C32'—C27'—C1'       | 124.3 (11) |
| O1—C4—C5            | 106.3 (4) | C29'—C28'—C27'      | 121.4 (13) |
| O1—C4—C3            | 112.3 (3) | C29'—C28'—H28'      | 119.3     |
| C5—C4—C3            | 109.9 (4) | C27'—C28'—H28'      | 119.3     |
| O1—C4—H4            | 109.4     | C28'—C29'—C30'      | 120.2 (12) |
| C5—C4—H4            | 109.4     | C28'—C29'—H29'      | 119.9     |
| C3—C4—H4            | 109.4     | C30'—C29'—H29'      | 119.9     |
| C4—C5—C6            | 113.6 (4) | C29'—C30'—C31'      | 124.3 (10) |
| C4—C5—H5A           | 108.8     | C29'—C30'—H30'      | 117.8     |
| C6—C5—H5A           | 108.8     | C31'—C30'—H30'      | 117.8     |
| C4—C5—H5B           | 108.8     | C30'—C31'—C32'      | 111.8 (10) |
| C6—C5—H5B           | 108.8     | C30'—C31'—H31'      | 124.1     |
| H5A—C5—H5B          | 107.7     | C32'—C31'—H31'      | 124.1     |
### Supporting Information

| Bond/Angle | Value | Bond/Angle | Value |
|------------|-------|------------|-------|
| N1—C6—C5  | 108.9 (5) | C31′—C32′—C27′ | 128.1 (11) |
| N1—C6—H6A | 109.9 | C31′—C32′—H32′ | 116.0 |
| C5—C6—H6A | 109.9 | C27′—C32′—H32′ | 116.0 |
| N1—C6—H6B | 109.9 | O4—C33—O3 | 124.3 (14) |
| C5—C6—H6B | 108.3 | O4—C33—C34 | 119.06 (14) |
| H6A—C6—H6B | 117.2 (17) | O3—C33—C34 | 116.56 (14) |
| C22—C21—C26 | 118.8 (4) | C35—C34—C33 | 123.21 (15) |
| C22—C21—C1 | 120.5 (4) | C35—C34—H34 | 118.4 |
| C26—C21—C1 | 120.7 (4) | C33—C34—H34 | 118.4 |
| C21—C22—C23 | 122.1 (4) | C34—C35—C36 | 120.84 (15) |
| C21—C22—H22 | 119.0 | C34—C35—H35 | 119.6 |
| C23—C22—H22 | 119.0 | C36—C35—H35 | 119.6 |
| C24—C23—C22 | 118.4 (3) | O6—C36—O5 | 121.01 (15) |
| C24—C23—H23 | 120.8 | O6—C36—C35 | 122.62 (15) |
| C22—C23—H23 | 120.8 | O5—C36—C35 | 116.37 (14) |
| C23—C24—C25 | 120.4 (4) | C36—O5—H5O | 108.7 (12) |
| C23—C24—H24 | 119.8 | | |

### Additional Bond/Angle Information

| Bond/Angle | Value |
|------------|-------|
| C7—C8—C9 | −171.8 (10) |
| N1—C7—C8—C9 | −178.7 (3) |
| C7—C8—C9—C10 | −168.02 (14) |
| C8—C9—C10—O2 | 1.6 (2) |
| C8—C9—C10—C11 | −179.52 (14) |
| C9—C10—C11—C16 | −177.72 (17) |
| C9—C10—C11—C16 | 3.4 (2) |
| C9—C10—C11—C12 | 2.4 (2) |
| C9—C10—C11—C12 | −176.43 (16) |
| C16—C11—C12—C13 | 0.0 (3) |
| C10—C11—C12—C13 | 179.89 (16) |
| C11—C12—C13—C14 | 0.4 (3) |
| C12—C13—C14—C15 | −0.5 (3) |
| C12—C13—C14—C17 | −176.41 (16) |
| C13—C14—C15—C16 | 0.1 (3) |
| C17—C14—C15—C16 | 176.04 (17) |
| C14—C15—C16—C11 | 0.3 (3) |
| C12—C11—C16—C15 | −0.4 (3) |
| C10—C11—C16—C15 | 179.75 (16) |
| C15—C14—C17—C18 | 148.79 (18) |
| C13—C14—C17—C18 | −35.5 (2) |
| C15—C14—C17—C20 | 27.4 (2) |
| C13—C14—C17—C20 | −156.94 (17) |
| C15—C14—C17—C19 | −91.8 (2) |
| C13—C14—C17—C19 | 83.9 (2) |
| C8—C7—N1—C6 | −153.5 (5) |
| C8—C7—N1—C2 | 83.3 (7) |
| C4—O1—C1—C27 | 175.6 (3) |
| C4—O1—C1—C21 | −60.0 (4) |
| C6—N1—C2—C3 | 61.7 (8) |
| Bond angle (°) | Value     | Bond angle (°) | Value     |
|---------------|-----------|---------------|-----------|
| C7—N1—C2—C3  | −173.2 (5) | C26′—C21′—C22′—C23′ | −29 (2) |
| N1—C2—C3—C4  | −56.4 (7)  | C1′—C21′—C22′—C23′ | 170.0 (13) |
| C1—O1—C4—C5  | 177.4 (3)  | C21′—C22′—C23′—C24′ | 10 (3)  |
| C1—O1—C4—C5  | −62.3 (4)  | C22′—C23′—C24′—C25′ | 7 (4)   |
| C2—C3—C4—O1  | −67.9 (6)  | C23′—C24′—C25′—C26′ | −7 (4)  |
| C2—C3—C4—C5  | 50.2 (6)   | C22′—C21′—C26′—C25′ | 28 (2)  |
| O1—C4—C5—C6  | 70.8 (6)   | C1′—C21′—C26′—C25′ | −169.2 (14) |
| N1—C2—C3—C4  | 56.4 (7)   | C24′—C25′—C26′—C21′ | −11 (3) |
| C1—O1—C4—C3  | 62.3 (4)   | C22′—C23′—C24′—C25′ | 7 (4)   |
| C2—C3—C4—C5  | −67.9 (6)  | C23′—C24′—C25′—C26′ | −7 (4)  |
| C2—C3—C4—C5  | 50.2 (6)   | C22′—C21′—C26′—C25′ | 28 (2)  |
| O1—C4—C5—C6  | 70.8 (6)   | C1′—C21′—C26′—C25′ | −169.2 (14) |
| N1—C2—C3—C4  | 56.4 (7)   | C24′—C25′—C26′—C21′ | −11 (3) |
| C1—O1—C4—C3  | 62.3 (4)   | C22′—C23′—C24′—C25′ | 7 (4)   |
| C2—C3—C4—C5  | −67.9 (6)  | C23′—C24′—C25′—C26′ | −7 (4)  |
| C2—C3—C4—C5  | 50.2 (6)   | C22′—C21′—C26′—C25′ | 28 (2)  |
| O1—C4—C5—C6  | 70.8 (6)   | C1′—C21′—C26′—C25′ | −169.2 (14) |
| N1—C2—C3—C4  | 56.4 (7)   | C24′—C25′—C26′—C21′ | −11 (3) |
| C1—O1—C4—C3  | 62.3 (4)   | C22′—C23′—C24′—C25′ | 7 (4)   |
| C2—C3—C4—C5  | −67.9 (6)  | C23′—C24′—C25′—C26′ | −7 (4)  |
| C2—C3—C4—C5  | 50.2 (6)   | C22′—C21′—C26′—C25′ | 28 (2)  |
| O1—C4—C5—C6  | 70.8 (6)   | C1′—C21′—C26′—C25′ | −169.2 (14) |
| N1—C2—C3—C4  | 56.4 (7)   | C24′—C25′—C26′—C21′ | −11 (3) |
| C1—O1—C4—C3  | 62.3 (4)   | C22′—C23′—C24′—C25′ | 7 (4)   |
| C2—C3—C4—C5  | −67.9 (6)  | C23′—C24′—C25′—C26′ | −7 (4)  |
| C2—C3—C4—C5  | 50.2 (6)   | C22′—C21′—C26′—C25′ | 28 (2)  |
| O1—C4—C5—C6  | 70.8 (6)   | C1′—C21′—C26′—C25′ | −169.2 (14) |
| N1—C2—C3—C4  | 56.4 (7)   | C24′—C25′—C26′—C21′ | −11 (3) |
| C1—O1—C4—C3  | 62.3 (4)   | C22′—C23′—C24′—C25′ | 7 (4)   |
| C2—C3—C4—C5  | −67.9 (6)  | C23′—C24′—C25′—C26′ | −7 (4)  |
| C2—C3—C4—C5  | 50.2 (6)   | C22′—C21′—C26′—C25′ | 28 (2)  |
| O1—C4—C5—C6  | 70.8 (6)   | C1′—C21′—C26′—C25′ | −169.2 (14) |

Hydrogen-bond geometry (Å, °)

Hydrogen-bond geometry (Å, °)

| Bond angle (°) | Value     | Bond angle (°) | Value     |
|---------------|-----------|---------------|-----------|
| Cg1 and Cg2 represent the centroids of phenyl rings C21–C26 and C27–C32, respectively. |

| Hydrogen-bond geometry (Å, °) | D—H···A | D—H | H···A | D···A | D—H···A |
|------------------------------|---------|-----|-------|-------|---------|
| N1—H1N···O4                  | 0.95    | 1.75| 2.697 (11) | 175 |
| N1′—H1N···O4                 | 1.00    | 1.78| 2.77 (3)   | 169 |
| O5—H50···O3i                 | 1.04 (2) | 1.50 (2) | 2.5402 (17) | 171 (2) |
| C7—H74···O2ii                | 0.99    | 2.37| 3.330 (2)  | 164 |
| C8—H8B···O6iii               | 0.99    | 2.53| 3.325 (2)  | 137 |
| C34—H34···O5iv               | 0.95    | 2.62| 3.208 (2)  | 121 |
| C35—H35···O3i                | 0.95    | 2.49| 3.1450 (19) | 127 |
| C31—H31···Cg1iv              | 0.95    | 2.72| 3.534 (6)  | 145 |
| C25—H25···Cg1v               | 0.95    | 2.70| 3.532 (4)  | 146 |
| C23—H23···Cg2iv              | 0.95    | 2.75| 3.624 (4)  | 154 |

Symmetry codes: (i) x, y+1, z; (ii) x, y−1, z; (iii) x, −y+5/2, z+1/2; (iv) −x+1, −y, −z; (v) −x+1, y−1/2, −z−1/2; (vi) −x+1, −y+1, −z.

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