The methanol and ethanol solvates of 4-glutarato-\(N,N\)-diisopropyltryptamine

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The solid-state structures of two solvated forms of 4-glutarato-\(N,N\)-diisopropyltryptamine were determined by single-crystal X-ray diffraction, namely, 5-[(3-{2-[bis(propan-2-yl)azaniumyl]ethyl}-1H-indol-4-yl)oxy]-5-oxopentanoate methanol monosolvate, \(C_{21}H_{30}N_2O_4\)/\(C_1CH_3OH\), and the analogous ethanol monosolvate, \(C_{21}H_{30}N_2O_4\)/\(C_1C_2H_6O\). In both compounds, the 4-glutarato-\(N,N\)-diisopropyltryptamine exists as a zwitterion with a protonated tertiary ammonium and a deprotonated glutarato carboxylate. The tryptamine zwitterions and alcohol solvates in both structures combine to produce near identical hydrogen-bonding networks, with N—H···O and O—H···O hydrogen bonds joining the molecules together in two-dimensional networks parallel to the (100) plane.

1. Chemical context

Psychedelic compounds continue to be a major research focus for treating conditions including depression, post-traumatic stress disorder (PTSD), Alzheimer’s disease, and chronic pain (Carhart-Harris & Goodwin, 2017; Krediet et al., 2020; Vann Jones & O’Kelly, 2020; Ramaekers et al., 2021). Tryptamine compounds with chemical structures resembling that of the active product of magic mushrooms, psilocin (4-hydroxy-\(N,N\)-dimethyltryptamine; 4-HO-DMT), are of particular interest. This is due not just to their structural similarities to the neurotransmitter serotonin (5-hydroxytryptamine; 5-HT), but because many have desirable drug characteristics including oral availability, lowered susceptibility to monoamine oxidase (MAO) degradation, and short duration of action (Kuypers et al., 2019). The synthesis of prodrugs that undergo hydrolysis to produce 4-hydroxy derivatives of dialkyltryptamines are of increasing interest (Klein et al., 2021; Chadeayne et al., 2019; Chadeayne, Pham, Reid et al., 2020; Naeem et al., 2022).

4-Hydroxy-\(N,N\)-diisopropyltryptamine (4-HO-DiPT) is one example of a psilocin analog, first synthesized in 1977, in which both methyl groups on the ethylamino moiety of psilocin are replaced with isopropyl groups (Repke et al., 1977). In early 2022, 4-HO-DiPT along with four other psychedelics were part of a proposal issued by the US Drug Enforcement Administration (DEA), requesting comments on reclassifying these compounds to Schedule I of the Controlled Substance Act. Due to a strong public response, the DEA withdrew the proposal before the hearing, which was scheduled for August (US DEA, January 14 & July 6, 2022a,b).

4-HO-DiPT is a serotonin-2A (5-HT\(_{2A}\)) receptor agonist that, like psilocin, produces a head-twitch response (HTR) in...
mice, indicating its competence in producing psychedelic effects (Halberstadt et al., 2020). 4-HO-DiPT also interacts with the serotonin transporter (SERT) with IC<sub>50</sub> values in the low micromolar range, similar to 3,4-methylenedioxy-methamphetamine (MDMA) (Rickli et al., 2016). 4-HO-DiPT has been reported as orally active at a 15–20 mg dose, with its profound psychedelic effects beginning within 15 minutes and lasting about 2–3 h (Shulgin & Shulgin, 2017).

4-HO-DiPT glutarate, a ‘hemiester’ prodrug of 4-HO-DiPT has been reported in the patent literature (Bryson, 2022). We have previously published work characterizing tryptamine compounds, highlighting the importance of single-crystal X-ray diffraction studies when characterizing tryptamine salts because they can occur in a variety of forms that are often not appreciated by other means of characterization (Chadeayne et al., 2019a,b; Chadeayne, Pham, Golen et al., 2020; Sammeta et al., 2020; Pham et al., 2021; Naeem et al., 2022). To this end, we synthesized 4-glutarato-N,N-diisopropyltrypamine and report herein two crystalline forms of the compound as both its methanol and ethanol solvates.

2. Structural commentary

In the solid state, the compound exists as a zwitterion, with a protonated tertiary ammonium group and a deprotonated carboxylate of the glutarato group. Both of the solvate structures possess one zwitterionic molecule and one alcohol molecule in the asymmetric unit (Fig. 1). In the ethanol solvate, the alcohol molecule is disordered over two orientations in a 0.531 (11):0.469 (11) ratio. Both solvates have near planar indole units with r.m.s. deviations from planarity of 0.009 and 0.016 Å for the methanol and ethanol solvates, respectively. The glutarato units are also close to planar with r.m.s. deviations of only 0.061 and 0.071 Å. In both cases, the glutarato unit is nearly orthogonal to the indole plane, showing plane-to-plane twists of 90.99 (6) and 94.21 (8)°. Likewise, the ethylamino arms are nearly orthogonal to the indole plane with C7—C8—C9—C10 angles of 90.2 (2) and 86.1 (3)°. Both ethylamino arms demonstrate anti configurations, with C8—C9—C10—N2 angles of 179.92 (14) and 180.0 (2)°. In both structures, the glutarato and ethylamino arms are turned to opposite sides of the indole. This differs from the structures observed in other zwitterionic indoles where intramolecular hydrogen bonding leads to two groups being on the same side of the aromatic rings (Naeem et al., 2022). The nature of the groups in this compound only allows for intermolecular interactions (vide infra) and having the groups on opposite sides of the indole is sterically preferred.

3. Supramolecular features

In both crystals, the zwitterionic molecules and alcohol solvents are held together by N<sup>+</sup>—H⋯O<sup>-</sup> and O—H⋯O hydrogen bonds that produce infinite two-dimensional networks parallel to the (100) plane. The most significant hydrogen bonds are N2—H2⋯O4 bonds between the diisopropyltryptammonium cation and the carboxylate anion of another zwitterionic molecule. These interactions form centrosymmetrical dimers, which form rings with graph-set notation of R<sub>2</sub><sup>2</sup>(28) (Etter et al., 1990). These dimers are shown in Fig. 2. The dimers are joined together through N1—

Figure 1
The molecular structures of 4-glutarato-N,N-diisopropyltrypamine as both its methanol (left) and ethanol (right) solvate, showing atomic labeling. Displacement ellipsoids are shown at the 50% probability level. Hydrogen bonds are shown as dashed lines. Dashed bonds indicate the minor occupancy disordered component in the ethanol solvate.

Figure 2
The ring formed by the dimerization of two zwitterionic 4-glutarato-N,N-diisopropyltrypamine molecules with graph set notation of R<sub>2</sub><sup>2</sup>(28). The image shown is from the methanol solvate. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding are omitted for clarity. Symmetry code: (i) 1 − x, 1 − y, 1 − z.
H1···O3 hydrogen bonds between the indole nitrogen and the other carboxylate oxygen. The alcohol oxygens also hydrogen bond to the carboxylate anion through O5—H5 bonds (Tables 1 and 2). The two structures demonstrate near identical hydrogen-bonding networks in the solid state, which can be seen in their packing diagrams (Fig. 3).

4. Database survey

There are three reported tryptamine structures possessing isopropyl groups on the ethylamino arm, all of which are N-methyl-N-isopropyl derivatives: N-methyl-N-isopropyltryptammonium hydrofumarate (Chadeayne, Pham, Golen et al., 2019: RONSOF) as well as the hydrofumarate (Chadeayne, Pham, Golen et al., 2019: RONSUL) and fumarate (Chadeayne, Pham, Golen et al., 2020: TUFQAP) of 4-hydroxy-N-methyl-N-isopropyltryptamine. There are six structures of 4-substituted esters of tryptamines in the literature, all of which are four-acetoxy derivatives: the hydrofumarate (Chadeayne et al., 2019a: HOClUH) and fumarate (Chadeayne et al., 2019b: XOFOO) of psilacetin (4-acetoxy-N,N-dimethyltryptamine), 4-acetoxy-N-methyl-N-ethyltryptammonium hydrofumarate (Pham et al., 2021: OJIQIK), 4-acetoxy-N-methyl-N-allyltryptammonium hydrofumarate (Pham et al., 2021: OJIQQO), 4-acetoxy-N,N-diallyltryptammonium fumarate fumaric acid (Pham et al., 2021: OJIQUW), and 4-acetoxy-N,N,N-trimethyltryptammonium iodide (Chadeayne, Pham, Reid et al., 2020: XUXDUS). There are two tryptamine zwitterions reported in the literature, those being the natural products baecocystin, 4-phosphoryloxy-N,N-methyltryptamine (Naeem et al., 2022), and psilocybin, 4-phosphoryloxy-N,N-dimethyltryptamine (Weber & Petcher, 1974; PSILOC; Sherwood et al., 2022: TAVZID, TAVZID01; Greenan et al., 2020; OKOKAD).

5. Synthesis and crystallization

112 mg of 4-hydroxy-N,N-diisopropyltryptamine (1 mmol) were dissolved in 5 mL of chloroform. 0.3 mL of triethylamine (5 mmol) followed by 490 mg of glutaric anhydride (10 mmol) were then added to the solution. The mixture was stirred at room temperature for 30 minutes, resulting in a precipitate which was isolated via filtration. The precipitate was triturated with tetrahydrofuran and washed with chloroform to obtain 73 mg of white powder (65% yield).

1H NMR (400 MHz, DMSO-<sub>d6</sub>): δ 11.02 (s, 1H, NH), 7.22 (d, J = 8.1 Hz, 1H, ArH), 7.16 (d, J = 2.3 Hz, 1H, ArH), 6.64 (d, J = 7.5 Hz, 1H, ArH), 3.10 (sept, J = 6.5 Hz, 2H, CH<sub>2</sub>), 2.77–2.63 (m, 6H, CH<sub>2</sub>), 1.88 (t, J = 7.2 Hz, 2H, CH<sub>2</sub>), 1.00 (d, J = 6.6 Hz, 12H, CH<sub>3</sub>).

The powder was recrystallized from boiling methanol to yield single crystals of the methanol solvate suitable for X-ray diffraction analysis. Slow evaporation of an ethanol solution of the powder produced single crystals of the ethanol solvate suitable for X-ray diffraction analysis.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. In the methanol solvate, hydrogen atoms H1, H2 and H5A were found in a difference-Fourier map and in the ethanol solvate, hydrogen atoms H1 and H2 were found in a difference-Fourier map. These hydrogens were refined isotropically, using DFIX restraints with N—H(indole) distances of 0.87 (1) Å, N—H(ammonium) distances of 0.90 (1) Å, and O—H distances of 0.99 (1) Å. Isotropic displacement parameters were set to 1.2U<sub:eq</sub> of the parent nitrogen atoms and 1.5U<sub:eq</sub> of the parent oxygen atom. All other hydrogens were placed in calculated positions [C—H = 0.93 Å (sp<sup>3</sup>), 0.97 Å (CH<sub>2</sub>), 0.96 Å (CH<sub>3</sub>)]. The hydrogen atoms in the disordered ethanol molecule were placed in calculated positions [O—H = 0.82 Å]. Isotropic displacement parameters were set to 1.2U<sub:eq</sub> of the parent carbon atoms and 1.5U<sub:eq</sub> of the parent oxygen atoms.

### Table 1

| Hydrogen-bond geometry (Å, °) for the methanol solvate. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| D—H···A         | D—H             | D···A           | D—H···A         |
| O5—H5A···O4     | 1.00 (1)         | 1.83 (2)        | 2.748 (2)       | 151 (3)         |
| N2—H2···O4<sup>i</sup> | 0.90 (1)        | 1.81 (1)        | 2.7154 (19)     | 177 (2)         |
| N1—H1···O3<sup>iii</sup> | 0.86 (1)        | 1.99 (1)        | 2.773 (2)       | 151 (2)         |

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

### Table 2

| Hydrogen-bond geometry (Å, °) for the ethanol solvate. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| D—H···A         | D—H             | D···A           | D—H···A         |
| N2—H2···O4<sup>i</sup> | 0.90 (3)        | 1.79 (3)        | 2.686 (3)       | 177 (3)         |
| N1—H1···O3<sup>iii</sup> | 0.85 (1)        | 1.91 (1)        | 2.751 (3)       | 167 (3)         |
| O5—H5A···O4<sup>iii</sup> | 0.82           | 1.97            | 2.692 (10)      | 147             |
| O5A—H5AA···O4<sup>iii</sup> | 0.82           | 1.95            | 2.732 (6)       | 160             |

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

Figure 3

The crystal packing of the methanol solvate (left) and the ethanol solvate (right) of 4-glutarato-N,N-diisopropyltryptamine, both shown along the a-axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding are omitted for clarity.
Table 3
Experimental details

| Methanol solvate | Ethanol solvate |
|------------------|-----------------|
| Chemical data    |                 |
| Chemical formula | C₂₁H₃₀N₂O₄.CH₄.O| C₂₁H₃₀N₂O₄.C₂H₅.O |
| M₂              | 406.51          | 420.54               |
| Crystal system, space group | Monoclinic, P2₁/c | Monoclinic, P2₁/c |
| Temperature (K)  | 297             | 297                  |
| a, b, c (Å)      | 7.9531 (5), 13.4224 (7), 21.2015 (11) | 8.0087 (12), 13.7968 (17), 21.878 (3) |
| β (°)            | 92.484 (2)      | 90.749 (4)           |
| V (Å³)          | 2261.1 (2)      | 2417.2 (5)           |
| Z                | 4               | 4                    |
| Radiation type   | Mo Ka           | Mo Ka                |
| μ (mm⁻¹)        | 0.08            | 0.08                 |
| Crystal size (mm)| 0.22 × 0.21 × 0.20 | 0.30 × 0.27 × 0.22 |

Data collection
Diffractometer    Bruker D8 Venture CMOS    Bruker D8 Venture CMOS
Absorption correction Multi-scan (SADABS: Bruker, 2021) Multi-scan (SADABS: Bruker, 2021)
Iₘₘₙ, Iₘₜₙ 0.718, 0.745 0.692, 0.745
No. of measured, independent and observed [I > 2σ(I)] reflections 37412, 4461, 3038
Rₚ 0.039 0.055
(sin θ/λ)ₘₚₚ (Å⁻¹) 0.610 0.604
Refinement
R[F² > 2σ(F²)], wR(F²), S 0.050, 0.143, 1.03 0.060, 0.176, 1.04
No. of reflections 4304 4461
No. of parameters 279 313
No. of restraints 3 46
H-atom treatment H atoms treated by a mixture of independent and constrained refinement H atoms treated by a mixture of independent and constrained refinement
Δρₚₚₚₚ max, Δρₚₚₚₚ min (e Å⁻³) 0.46, −0.39 0.35, −0.46

Computer programs: APEX4 and SAINT (Bruker, 2021), SHELXT2014 (Sheldrick, 2015), SHELXL2018 (Sheldrick, 2015b), OLEX2 (Dolomanov et al., 2009), and pubCIF (Westrip, 2010).

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Computing details

For both structures, data collection: \textit{APEX4} (Bruker, 2021); cell refinement: \textit{SAINT} (Bruker, 2021); data reduction: \textit{SAINT} (Bruker, 2021); program(s) used to solve structure: \textit{SHELXT2014} (Sheldrick, 2015a); program(s) used to refine structure: \textit{SHELXL2018} (Sheldrick, 2015b); molecular graphics: \textit{OLEX2} (Dolomanov \textit{et al.}, 2009); software used to prepare material for publication: \textit{publCIF} (Westrip, 2010).

5-[(3-[2-[Bis(propan-2-yl)azaniumyl]ethyl]-1H-indol-4-yl)oxy]-5-oxopentanoate methanol monosolvate (I)

Crystal data

\[
\begin{align*}
C_{21}H_{30}N_2O_4 \cdot CH_4O \\
M_r &= 406.51 \\
\text{Monoclinic, } P2_1/c \\
a &= 7.9531 (5) \text{ Å} \\
b &= 13.4224 (7) \text{ Å} \\
c &= 21.2015 (11) \text{ Å} \\
\beta &= 92.484 (2) \text{°} \\
V &= 2261.1 (2) \text{ Å}^3 \\
Z &= 4 \\
F(000) &= 880 \\
D_a &= 1.194 \text{ Mg m}^{-3} \\
\text{Mo Ka radiation, } \lambda &= 0.71073 \text{ Å} \\
\text{Cell parameters from 9859 reflections} \\
\theta &= 3.0-25.6\text{°} \\
\mu &= 0.08 \text{ mm}^{-1} \\
T &= 297 \text{ K} \\
\text{Block, colourless} \\
0.22 \times 0.21 \times 0.20 \text{ mm}
\end{align*}
\]

Data collection

\text{Bruker D8 Venture CMOS diffractometer} \\
\varphi \text{ and } \omega \text{ scans} \\
Absorption correction: \text{multi-scan} \\
\text{(SADABS; Bruker, 2021)} \\
\text{4304 independent reflections} \\
3531 reflections with \(I > 2\sigma(I)\) \\
\(R_{\text{int}} = 0.039\) \\
\(\theta_{\text{max}} = 25.7\text{°}, \theta_{\text{min}} = 3.0\text{°}\) \\
\(h = -9 \rightarrow 9\) \\
\(k = -16 \rightarrow 16\) \\
\(l = -25 \rightarrow 25\) \\
61210 measured reflections

Refinement

Refinement on \(F^2\) \\
Least-squares matrix: full \\
\(R(F^2 > 2\sigma(F^2)) = 0.050\) \\
\(wR(F^2) = 0.143\) \\
\(S = 1.03\) \\
4304 reflections \\
279 parameters \\
3 restraints \\
Hydrogen site location: mixed \\
H atoms treated by a mixture of independent and constrained refinement \\
\(w = 1/[\sigma^2(F_c^2) + (0.0677P)^2 + 1.0658P]\) \\
where \(P = (F_c^2 + 2F_w^2)/3\) \\
\((\Delta\sigma)_{\text{max}} < 0.001\) \\
\(\Delta\rho_{\text{max}} = 0.46 \text{ e Å}^{-3}\) \\
\(\Delta\rho_{\text{min}} = -0.39 \text{ e Å}^{-3}\) \\
Extinction correction: \text{SHELXL2018} \\
(Sheldrick, 2015b), \\
\(\text{Fc}^2 = \text{KFc}[1 + 0.001x\text{Fc}^2\lambda^2/\sin(2\theta)]^{1/4}\) \\
Extinction coefficient: 0.0049 (16)
**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 (Å²)**

| Atom | x     | y     | z     | Uiso*/U(eq) |
|------|-------|-------|-------|-------------|
| O1   | 0.17552 (17) | 0.35382 (9) | 0.29846 (5) | 0.0421 (3) |
| O2   | 0.2385 (2) | 0.51443 (11) | 0.28621 (6) | 0.0675 (5) |
| O3   | 0.3521 (2) | 0.72404 (12) | 0.48361 (7) | 0.0730 (5) |
| O4   | 0.2931 (2) | 0.66404 (11) | 0.57648 (6) | 0.0621 (4) |
| N1   | 0.4481 (2) | 0.26115 (12) | 0.11776 (7) | 0.0454 (4) |
| N2   | 0.61740 (18) | 0.15461 (10) | 0.37628 (6) | 0.0362 (3) |
| C1   | 0.5573 (2) | 0.25778 (14) | 0.16893 (9) | 0.0446 (4) |
| H1A  | 0.669647 | 0.238884 | 0.167694 | 0.053* |
| C2   | 0.2940 (2) | 0.29148 (13) | 0.13645 (8) | 0.0386 (4) |
| C3   | 0.1426 (3) | 0.30411 (15) | 0.10225 (8) | 0.0481 (5) |
| C4   | 0.134321 | 0.291932 | 0.059041 | 0.058* |
| C5   | 0.0058 (3) | 0.33510 (17) | 0.13421 (9) | 0.0539 (5) |
| C6   | −0.096839 | 0.343720 | 0.112189 | 0.065* |
| C7   | 0.0169 (2) | 0.35412 (15) | 0.19936 (9) | 0.0489 (5) |
| H5   | −0.077222 | 0.375904 | 0.219944 | 0.059* |
| C8   | 0.1662 (2) | 0.34057 (12) | 0.23242 (8) | 0.0375 (4) |
| C9   | 0.3099 (2) | 0.30850 (12) | 0.20252 (7) | 0.0348 (4) |
| H10A | 0.4801 (2) | 0.28580 (12) | 0.22217 (8) | 0.0381 (4) |
| C10  | 0.5583 (2) | 0.27857 (13) | 0.28772 (8) | 0.0410 (4) |
| H9A  | 0.501378 | 0.323224 | 0.315755 | 0.049* |
| H9B  | 0.675960 | 0.297597 | 0.287599 | 0.049* |
| C11  | 0.5426 (2) | 0.17173 (13) | 0.31047 (8) | 0.0387 (4) |
| H10A | 0.424472 | 0.153645 | 0.309562 | 0.046* |
| H10B | 0.598183 | 0.128085 | 0.281434 | 0.046* |
| C12  | 0.4906 (2) | 0.10852 (14) | 0.41929 (9) | 0.0452 (4) |
| H11  | 0.547211 | 0.100130 | 0.460941 | 0.054* |
| C13  | 0.3444 (3) | 0.17846 (17) | 0.42725 (11) | 0.0581 (5) |
| H13A | 0.385521 | 0.241480 | 0.442784 | 0.087* |
| H13B | 0.269327 | 0.150484 | 0.456783 | 0.087* |
| H13C | 0.285274 | 0.187901 | 0.387253 | 0.087* |
| C14  | 0.3437 (4) | 0.00616 (17) | 0.39679 (13) | 0.0723 (7) |
| H12A | 0.530499 | −0.037275 | 0.396077 | 0.108* |
| H12B | 0.383512 | 0.011193 | 0.355068 | 0.108* |
| H12C | 0.354637 | −0.020317 | 0.424972 | 0.108* |
| C15  | 0.7823 (2) | 0.09675 (15) | 0.37460 (9) | 0.0471 (5) |
| H14  | 0.759363 | 0.032539 | 0.353974 | 0.057* |
| C15  | 0.8546 (3) | 0.0769 (2) | 0.44071 (11) | 0.0712 (7) |
| H15A | 0.783385 | 0.030922 | 0.461678 | 0.107* |
| H15B | 0.861037 | 0.138280 | 0.463944 | 0.107* |

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|       | x (Å)       | y (Å)       | z (Å)       | U11 (Å²) | U22 (Å²) | U33 (Å²) | U12 (Å²) | U13 (Å²) | U23 (Å²) |
|-------|-------------|-------------|-------------|----------|----------|----------|----------|----------|----------|
| O1    | 0.0613 (8)  | 0.0378 (6)  | 0.0278 (6)  | -0.0046 (6) | 0.0104 (5) | -0.0059 (5) |
| O2    | 0.1172 (14) | 0.0483 (8)  | 0.0375 (7)  | -0.0279 (9) | 0.0073 (8) | 0.0011 (6)  |
| O3    | 0.1127 (14) | 0.0647 (10) | 0.0436 (8)  | -0.0400 (9) | 0.0275 (8) | -0.0135 (7) |
| O4    | 0.1033 (12) | 0.0526 (8)  | 0.0311 (7)  | -0.0267 (8) | 0.0110 (7) | -0.0100 (6) |
| N1    | 0.0607 (10) | 0.0477 (9)  | 0.0289 (7)  | 0.0035 (7)  | 0.0133 (7) | -0.0045 (6) |
| N2    | 0.0427 (8)  | 0.0336 (7)  | 0.0321 (7)  | -0.0030 (6) | -0.0009 (6) | -0.0024 (6) |
| C1    | 0.0484 (10) | 0.0436 (10) | 0.0421 (10) | 0.0040 (8)  | 0.0068 (8) | -0.0017 (8) |
| C2    | 0.0537 (10) | 0.0338 (8)  | 0.0286 (8)  | -0.0027 (7) | 0.0058 (7) | -0.0025 (6) |
| C3    | 0.0624 (12) | 0.0538 (11) | 0.0278 (8)  | -0.0041 (9) | -0.0028 (8) | -0.0026 (8) |
| C4    | 0.0502 (11) | 0.0655 (13) | 0.0452 (11) | -0.0023 (10) | -0.0074 (9) | 0.0017 (9) |
| C5    | 0.0455 (10) | 0.0558 (11) | 0.0460 (11) | 0.0010 (9)  | 0.0075 (8) | -0.0030 (9) |
| C6    | 0.0500 (10) | 0.0347 (8)  | 0.0283 (8)  | -0.0044 (7) | 0.0073 (7) | -0.0033 (6) |
| C7    | 0.0476 (9)  | 0.0301 (8)  | 0.0266 (8)  | -0.0030 (7) | 0.0026 (7) | -0.0017 (6) |
| C8    | 0.0480 (10) | 0.0333 (8)  | 0.0331 (8)  | -0.0006 (7) | 0.0028 (7) | -0.0002 (7) |
| C9    | 0.0477 (10) | 0.0379 (9)  | 0.0370 (9)  | -0.0015 (7) | -0.0027 (7) | -0.0032 (7) |
| C10   | 0.0440 (9)  | 0.0398 (9)  | 0.0318 (8)  | -0.0042 (7) | -0.0027 (7) | -0.0033 (7) |
| C11   | 0.0531 (11) | 0.0423 (10) | 0.0404 (9)  | -0.0060 (8) | 0.0054 (8) | 0.0046 (8) |
| C12   | 0.0523 (12) | 0.0638 (13) | 0.0592 (13) | -0.0052 (10) | 0.0121 (10) | -0.0035 (10) |
| C13   | 0.0905 (18) | 0.0434 (12) | 0.0845 (17) | -0.0185 (12) | 0.0207 (14) | 0.0013 (11) |
| C14   | 0.0463 (10) | 0.0472 (10) | 0.0475 (10) | 0.0064 (8)  | -0.0030 (8) | -0.0041 (8) |

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Geometric parameters (Å, °)

| Bond/Angle | Length/Distance | Value | Value | Value | Value | Value | Value |
|------------|----------------|-------|-------|-------|-------|-------|-------|
| O1—C6      |                | 1.4100 (19) |       |       |       |       |       |
| O1—C17     |                | 1.358 (2) |       |       |       |       |       |
| O1—C17     |                | 1.182 (2) |       |       |       |       |       |
| O2—C17     |                | 1.182 (2) |       |       |       |       |       |
| O3—C21     |                | 1.242 (2) |       |       |       |       |       |
| O4—C21     |                | 1.259 (2) |       |       |       |       |       |
| N1—C1      |                | 1.361 (2) |       |       |       |       |       |
| N1—C2      |                | 1.366 (2) |       |       |       |       |       |
| N1—H1      |                | 0.862 (9) |       |       |       |       |       |
| N2—C10     |                | 1.510 (2) |       |       |       |       |       |
| N2—C11     |                | 1.406 (3) |       |       |       |       |       |
| N2—C14     |                | 1.520 (2) |       |       |       |       |       |
| N2—C14     |                | 1.520 (2) |       |       |       |       |       |
| C1—C8      |                | 1.501 (2) |       |       |       |       |       |
| C2—C3      |                | 1.501 (2) |       |       |       |       |       |
| C3—C4      |                | 1.390 (3) |       |       |       |       |       |
| C4—C5      |                | 1.501 (2) |       |       |       |       |       |
| C5—H5      |                | 0.9300   |       |       |       |       |       |
| C5—C6      |                | 1.390 (3) |       |       |       |       |       |
| C6—C7      |                | 1.390 (3) |       |       |       |       |       |
| C7—C8      |                | 1.390 (3) |       |       |       |       |       |
| C8—C9      |                | 1.501 (2) |       |       |       |       |       |
| C9—H9A     |                | 0.9700   |       |       |       |       |       |
| C9—H9B     |                | 0.9700   |       |       |       |       |       |
| C9—C10     |                | 1.520 (2) |       |       |       |       |       |
| C10—H10A   |                | 0.9700   |       |       |       |       |       |
| C10—H10B   |                | 0.9700   |       |       |       |       |       |
| C11—H11    |                | 0.9800   |       |       |       |       |       |
| C11—C13    |                | 1.510 (3) |       |       |       |       |       |

C17—O1—C17 C11—C13—H13C 109.5
C1—N1—C2 C11—C12—H12A 109.5
C1—N1—H1 C11—C12—H12B 109.5

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C2—N1—H1  
C10—N2—C11  
C10—N2—C14  
C10—N2—H2  
C11—N2—C14  
C11—N2—H2  
C11—N2—C14  
N1—C1—C8  
C8—C1—H1A  
N1—C2—C3  
N1—C2—C7  
C3—C2—C7  
C2—C3—H3  
C4—C3—C2  
C4—C3—H3  
C3—C4—H4  
C3—C4—C5  
C5—C4—H4  
C5—C4—C5  
C6—C5—C4  
C6—C5—H5  
C5—C6—O1  
C6—C7—C8  
C1—C8—C9  
C7—C8—C9  
C8—C9—H9A  
C8—C9—H9B  
C8—C9—C10  
H9A—C9—H9B  
C10—C9—H9A  
C10—C9—H9B  
N2—C10—C9  
N2—C10—H10A  
N2—C10—H10B  
C9—C10—H10A  
C9—C10—H10B  
H10A—C10—H10B  
N2—C11—H11  
C13—C11—N2  
C13—C11—H11  
C13—C11—C12  
C12—C11—N2

126.4 (15)  
111.80 (14)  
111.11 (13)  
106.6 (13)  
113.58 (14)  
106.8 (13)  
106.4 (13)  
124.6  
110.89 (17)  
124.6  
130.79 (16)  
106.95 (15)  
122.25 (17)  
121.1  
117.88 (17)  
121.1  
119.2  
121.60 (18)  
119.2  
120.1  
119.84 (18)  
120.1  
120.02 (16)  
121.21 (16)  
118.69 (15)  
107.19 (15)  
117.21 (16)  
135.60 (15)  
105.81 (15)  
124.48 (17)  
129.19 (15)  
110.0  
110.0  
108.57 (14)  
108.4  
110.0  
110.0  
113.72 (13)  
108.8  
108.8  
114.98 (16)  
108.8  
108.8  
108.8  
113.78 (16)  
108.5  
108.5  
114.98 (16)  
108.5  
122.88 (17)  
120.35 (16)  
116.77 (17)  
101 (2)  
109.5
C12–C11–H11 107.3  O5–C22–H22B 109.5
C11–C13–H13A 109.5  O5–C22–H22C 109.5
C11–C13–H13B 109.5  H22A–C22–H22B 109.5
C11–C13–H13C 109.5  H22A–C22–H22C 109.5
H13A–C13–H13B 109.5  H22B–C22–H22C 109.5
H13A–C13–H13C 109.5  

O1–C6–C7–C2 177.15 (14)  C6–O1–C17–C18 −2.0 (3)
O1–C6–C7–C8 −2.1 (3)  C6–O1–C17–O2 −179.77 (15)
O1–C17–C18–C19 −177.50 (17)  C6–C7–C8–C1 179.74 (19)
O2–C17–C18–C19 4.8 (3)  C6–C7–C8–C9 7.9 (3)
N1–C1–C8–C7 −0.1 (2)  C7–C2–C3–C4 0.7 (3)
N1–C1–C8–C9 172.23 (16)  C7–C8–C9–C10 90.2 (2)
N1–C2–C3–C4 179.42 (19)  C8–C9–C10–N2 179.92 (14)
N1–C2–C3–C4 −0.61 (19)  C10–N2–C11–C12 63.1 (2)
C1–N1–C2–C3 −178.34 (19)  C10–N2–C11–C13 −63.01 (19)
C1–N1–C2–C7 0.5 (2)  C10–N2–C11–C14 −51.2 (2)
C2–N1–C1–C8 −178.76 (19)  C10–N2–C14–C15 −178.31 (17)
C2–N1–C1–C8 0.45 (19)  C10–N2–C14–C16 −106.70 (17)
C2–C7–C8–C1 0.5 (2)  C14–N2–C10–C9 125.26 (16)
C2–C7–C8–C9 −171.42 (16)  C14–N2–C10–C19 58.79 (19)
C3–C2–C7–C6 −1.1 (2)  C14–N2–C10–C13 −51.2 (2)
C3–C2–C7–C8 178.39 (16)  C14–N2–C11–C13 170.27 (16)
C3–C4–C5–C6 −0.8 (3)  C14–N2–C11–C12 −63.6 (2)
C4–C5–C6–C7 178.20 (17)  C14–N2–C11–C12 −63.6 (2)
C4–C5–C6–O1 0.4 (3)  C17–O1–C6–C5 94.06 (19)
C5–C6–C7–C2 −178.76 (19)  C17–O1–C6–C7 −89.2 (2)
C5–C6–C7–C8 0.5 (2)  C17–C18–C19–C20 179.16 (18)
C5–C6–C7–C8 0.5 (2)  C17–C18–C19–C20 179.16 (18)

Hydrogen-bond geometry (Å, °)

| D—H···A    | D—H | H···A | D···A | D—H···A |
|------------|------|-------|-------|---------|
| O5—H5A···O4 | 1.00 (1) | 1.83 (2) | 2.748 (2) | 151 (3) |
| N2—H2···O4i  | 0.90 (1) | 1.81 (1) | 2.7154 (19) | 177 (2) |
| N1—H1···O3ii | 0.86 (1) | 1.99 (1) | 2.773 (2) | 151 (2) |

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

5-[(3-(-[Bis(propan-2-yl)azaniumyl]ethyl)-1H-indol-4-yl)oxy]-5-oxopentanoate ethanol monosolvate (II)

Crystal data

C21H30N2O4·C2H6O   V = 2417.2 (5) Å³
Mr = 420.54
Monoclinic, P21/c   Z = 4
a = 8.0087 (12) Å   µ(000) = 912
b = 13.7968 (17) Å   Dα = 1.156 Mg m⁻³
Monoclinic, P21/c   Mo Kα radiation, λ = 0.71073 Å
a = 8.0087 (12) Å   Cell parameters from 7678 reflections
b = 13.7968 (17) Å   θ = 2.5–24.9°
c = 21.878 (3) Å
β = 90.749 (4)°

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**Supporting Information**

\[\mu = 0.08 \text{ mm}^{-1}\]

\[T = 297 \text{ K}\]

**Block, colourless**

\[0.30 \times 0.27 \times 0.22 \text{ mm}\]

**Data Collection**

Bruker D8 Venture CMOS
diffractometer

\[\varphi \text{ and } \omega \text{ scans}\]

Absorption correction: multi-scan
(SADABS; Bruker, 2021)

\[T_{\text{min}} = 0.692, \ T_{\text{max}} = 0.745\]

37412 measured reflections

4461 independent reflections

3038 reflections with \(I > 2\sigma(I)\)

\[R_{\text{int}} = 0.055\]

\[\theta_{\text{max}} = 25.4^\circ, \ \theta_{\text{min}} = 2.5^\circ\]

\[h = -9 \rightarrow 9\]

\[k = -16 \rightarrow 16\]

\[l = -26 \rightarrow 26\]

**Refinement**

Refinement on \(F^2\)

Least-squares matrix: full

\[\text{R}[F^2 > 2\sigma(F^2)] = 0.060\]

\[wR(F^2) = 0.176\]

\[S = 1.04\]

4461 reflections

313 parameters

46 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

\[w = 1/\left[\sigma^2(F_o^2) + (0.0772P)^2 + 1.2353P\right]\]

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

\[\Delta\sigma_{\text{max}} < 0.001\]

\[\Delta\rho_{\text{max}} = 0.35 \text{ e Å}^{-3}\]

\[\Delta\rho_{\text{min}} = -0.46 \text{ e Å}^{-3}\]

**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 (Å²)**

|    |    |    |    |    |      |
|----|----|----|----|----|------|
| O1 | 0.2092 (2) | 0.36531 (11) | 0.30305 (7) | 0.0555 (5) |
| O2 | 0.2584 (3) | 0.52278 (14) | 0.28903 (8) | 0.0832 (7) |
| O3 | 0.3563 (3) | 0.73209 (16) | 0.48029 (8) | 0.0872 (7) |
| O4 | 0.2945 (3) | 0.67092 (14) | 0.56965 (8) | 0.0787 (7) |
| N1 | 0.4952 (3) | 0.27474 (16) | 0.12915 (9) | 0.0595 (6) |
| N2 | 0.6135 (3) | 0.16000 (15) | 0.37926 (9) | 0.0508 (5) |
| C1 | 0.5975 (4) | 0.26944 (19) | 0.17914 (11) | 0.0583 (7) |
| H1A | 0.708687 | 0.250056 | 0.178280 | 0.070* |
| C2 | 0.3413 (4) | 0.30442 (17) | 0.14673 (10) | 0.0513 (6) |
| C3 | 0.1947 (4) | 0.31751 (19) | 0.11340 (12) | 0.0630 (7) |
| H3 | 0.191217 | 0.307090 | 0.071410 | 0.076* |
| C4 | 0.0551 (4) | 0.3462 (2) | 0.14408 (13) | 0.0701 (8) |
| H4 | -0.044828 | 0.354362 | 0.122584 | 0.084* |
| C5 | 0.0599 (4) | 0.3635 (2) | 0.20711 (12) | 0.0628 (7) |
| H5 | -0.035912 | 0.383807 | 0.226972 | 0.075* |
| C6 | 0.2045 (3) | 0.35080 (17) | 0.23928 (10) | 0.0504 (6) |
| C7 | 0.3503 (3) | 0.31992 (15) | 0.21087 (10) | 0.0461 (6) |
| C8 | 0.5159 (3) | 0.29619 (16) | 0.23053 (10) | 0.0492 (6) |
| C9 | 0.5832 (3) | 0.28496 (17) | 0.29440 (11) | 0.0532 (6) |
| H9A | 0.528225 | 0.330228 | 0.321445 | 0.064* |
| Atom  | x     | y     | z     | Ueq  |
|-------|-------|-------|-------|-------|
| H9B   | 0.702044 | 0.298597 | 0.295389 | 0.064* |
| C10   | 0.5518 (3) | 0.18157 (17) | 0.31541 (10) | 0.0513 (6) |
| H10A  | 0.432721 | 0.168963 | 0.313271 | 0.062* |
| H10B  | 0.605720 | 0.137478 | 0.287333 | 0.062* |
| C11   | 0.7716 (4) | 0.0990 (2) | 0.37851 (13) | 0.0689 (8) |
| H11   | 0.745795 | 0.037954 | 0.357516 | 0.083* |
| C12   | 0.8324 (5) | 0.0750 (3) | 0.44274 (16) | 0.0990 (12) |
| H12A  | 0.753581 | 0.032798 | 0.461969 | 0.148* |
| H12B  | 0.843001 | 0.133711 | 0.466050 | 0.148* |
| C13   | 0.9059 (4) | 0.1506 (3) | 0.34291 (17) | 0.0903 (11) |
| H13A  | 0.866622 | 0.162243 | 0.301912 | 0.135* |
| H13B  | 1.004393 | 0.111058 | 0.341935 | 0.135* |
| H13C  | 0.931685 | 0.211311 | 0.362305 | 0.135* |
| C14   | 0.4773 (4) | 0.11792 (19) | 0.41877 (12) | 0.0615 (7) |
| H14   | 0.526311 | 0.106134 | 0.459368 | 0.074* |
| C15   | 0.4148 (5) | 0.0211 (2) | 0.39449 (17) | 0.0947 (12) |
| H15A  | 0.505966 | −0.023937 | 0.393021 | 0.142* |
| H15B  | 0.368656 | 0.029758 | 0.354130 | 0.142* |
| H15C  | 0.330151 | −0.003624 | 0.420973 | 0.142* |
| C16   | 0.3377 (4) | 0.1903 (2) | 0.42646 (14) | 0.0753 (9) |
| H16A  | 0.255515 | 0.164077 | 0.453397 | 0.113* |
| H16B  | 0.286909 | 0.203677 | 0.387375 | 0.113* |
| H16C  | 0.381923 | 0.249228 | 0.443505 | 0.113* |
| C17   | 0.2386 (3) | 0.45697 (18) | 0.32284 (11) | 0.0538 (6) |
| C18   | 0.2450 (4) | 0.46119 (18) | 0.39101 (11) | 0.0596 (7) |
| H18A  | 0.336436 | 0.420965 | 0.405661 | 0.072* |
| H18B  | 0.142255 | 0.434400 | 0.406826 | 0.072* |
| C19   | 0.2678 (4) | 0.56242 (19) | 0.41582 (11) | 0.0625 (7) |
| H19A  | 0.373719 | 0.587837 | 0.402005 | 0.075* |
| H19B  | 0.179984 | 0.603603 | 0.399319 | 0.075* |
| C20   | 0.2642 (4) | 0.5668 (2) | 0.48422 (11) | 0.0690 (8) |
| H20A  | 0.341419 | 0.518749 | 0.500346 | 0.083* |
| H20B  | 0.153216 | 0.548829 | 0.497359 | 0.083* |
| C21   | 0.3081 (4) | 0.6643 (2) | 0.51231 (11) | 0.0627 (7) |
| H2    | 0.640 (3) | 0.217 (2) | 0.3959 (12) | 0.064 (8)* |
| H1    | 0.526 (3) | 0.261 (2) | 0.0929 (6) | 0.068 (8)* |
| O5    | −0.1278 (12) | 0.4643 (7) | 0.3667 (5) | 0.123 (3) |
| H5A   | −0.165922 | 0.438097 | 0.397138 | 0.184* |
| C22   | −0.2489 (13) | 0.5309 (7) | 0.3417 (5) | 0.106 (3) |
| H22A  | −0.281815 | 0.577081 | 0.372735 | 0.127* |
| H22B  | −0.347635 | 0.495888 | 0.328047 | 0.127* |
| C23   | −0.1720 (13) | 0.5827 (6) | 0.2891 (3) | 0.106 (3) |
| H23A  | −0.251356 | 0.627541 | 0.271841 | 0.159* |
| H23B  | −0.074882 | 0.617423 | 0.303038 | 0.159* |
| H23C  | −0.140469 | 0.536518 | 0.258509 | 0.159* |
| O5A   | −0.1337 (9) | 0.4474 (4) | 0.3501 (3) | 0.0655 (18) |
| H5AA  | −0.198660 | 0.410977 | 0.367474 | 0.098* |
|     | \(U^{11}\)      | \(U^{22}\)      | \(U^{33}\)      | \(U^{12}\)      | \(U^{13}\)      | \(U^{23}\)      |
|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| O1  | 0.0813 (13)     | 0.0451 (9)      | 0.0399 (9)      | -0.0016 (8)     | 0.0149 (8)      | -0.0089 (7)     |
| O2  | 0.142 (2)       | 0.0566 (12)     | 0.0510 (11)     | -0.0251 (12)    | 0.0040 (12)     | 0.0006 (9)      |
| O3  | 0.142 (2)       | 0.0749 (13)     | 0.0456 (10)     | -0.0433 (13)    | 0.0284 (11)     | -0.0115 (10)    |
| O4  | 0.1303 (19)     | 0.0686 (12)     | 0.0376 (9)      | -0.0367 (12)    | 0.0170 (10)     | -0.0126 (8)     |
| N1  | 0.0858 (17)     | 0.0567 (13)     | 0.0364 (11)     | 0.0033 (11)     | 0.0155 (11)     | 0.0061 (9)      |
| N2  | 0.0669 (14)     | 0.0427 (11)     | 0.0428 (11)     | -0.0010 (10)    | 0.0009 (9)      | -0.0050 (9)     |
| C1  | 0.0704 (18)     | 0.0556 (15)     | 0.0491 (14)     | 0.0020 (13)     | 0.0113 (12)     | -0.0018 (11)    |
| C2  | 0.0757 (18)     | 0.0403 (12)     | 0.0382 (12)     | -0.0019 (12)    | 0.0086 (12)     | -0.0034 (10)    |
| C3  | 0.090 (2)       | 0.0592 (16)     | 0.0391 (13)     | -0.0040 (15)    | -0.0046 (14)    | -0.0045 (11)    |
| C4  | 0.075 (2)       | 0.0740 (19)     | 0.0604 (17)     | -0.0038 (16)    | -0.0109 (15)    | -0.0013 (14)    |
| C5  | 0.0634 (18)     | 0.0629 (17)     | 0.0621 (16)     | 0.0023 (13)     | 0.0069 (14)     | -0.0077 (13)    |
| C6  | 0.0693 (17)     | 0.0428 (13)     | 0.0392 (12)     | -0.0041 (11)    | 0.0078 (11)     | -0.0071 (10)    |
| C7  | 0.0662 (16)     | 0.0360 (11)     | 0.0360 (11)     | -0.0054 (10)    | 0.0050 (10)     | -0.0042 (9)     |
| C8  | 0.0650 (16)     | 0.0410 (12)     | 0.0417 (12)     | -0.0040 (11)    | 0.0050 (11)     | -0.0024 (10)    |
| C9  | 0.0671 (17)     | 0.0480 (14)     | 0.0444 (13)     | -0.0043 (12)    | 0.0013 (11)     | -0.0063 (10)    |
| C10 | 0.0649 (16)     | 0.0482 (14)     | 0.0407 (12)     | -0.0041 (12)    | -0.0010 (11)    | -0.0045 (10)    |
| C11 | 0.078 (2)       | 0.0663 (18)     | 0.0619 (16)     | 0.0174 (15)     | -0.0067 (14)    | -0.0074 (14)    |
| C12 | 0.103 (3)       | 0.113 (3)       | 0.080 (2)       | 0.033 (2)       | -0.021 (2)      | 0.003 (2)       |
| C13 | 0.066 (2)       | 0.112 (3)       | 0.094 (2)       | 0.0162 (19)     | 0.0070 (18)     | -0.011 (2)      |
| C14 | 0.081 (2)       | 0.0516 (14)     | 0.0520 (14)     | -0.0085 (14)    | 0.0075 (13)     | 0.0042 (12)     |
| C15 | 0.126 (3)       | 0.0562 (18)     | 0.102 (3)       | -0.0246 (19)    | 0.022 (2)       | 0.0006 (17)     |
| C16 | 0.078 (2)       | 0.076 (2)       | 0.0728 (19)     | -0.0069 (16)    | 0.0166 (16)     | -0.0036 (15)    |
| C17 | 0.0651 (17)     | 0.0494 (14)     | 0.0470 (13)     | -0.0051 (12)    | 0.0068 (11)     | -0.0079 (11)    |
| C18 | 0.0809 (19)     | 0.0515 (14)     | 0.0466 (14)     | -0.0031 (13)    | 0.0096 (13)     | -0.0091 (11)    |
| C19 | 0.083 (2)       | 0.0556 (15)     | 0.0487 (14)     | -0.0081 (14)    | 0.0050 (13)     | -0.0121 (12)    |
| C20 | 0.098 (2)       | 0.0628 (17)     | 0.0465 (14)     | -0.0181 (15)    | 0.0105 (14)     | -0.0130 (12)    |
| C21 | 0.084 (2)       | 0.0624 (16)     | 0.0420 (13)     | -0.0190 (14)    | 0.0143 (13)     | -0.0109 (12)    |
| C5  | 0.125 (4)       | 0.120 (4)       | 0.123 (4)       | 0.0016 (19)     | 0.0008 (19)     | 0.0101 (19)     |
| C22 | 0.106 (3)       | 0.105 (3)       | 0.107 (3)       | 0.0010 (10)     | 0.0003 (10)     | -0.0001 (10)    |
| C23 | 0.107 (3)       | 0.104 (3)       | 0.106 (3)       | 0.0061 (19)     | 0.0028 (19)     | 0.0021 (19)     |
| O5  | 0.070 (2)       | 0.060 (2)       | 0.067 (2)       | -0.0011 (15)    | 0.0075 (16)     | 0.0087 (16)     |
| C22A| 0.098 (3)       | 0.096 (3)       | 0.099 (3)       | 0.0021 (10)     | 0.0001 (10)     | 0.0004 (10)     |
| C23A| 0.098 (4)       | 0.094 (3)       | 0.100 (3)       | 0.0024 (19)     | -0.0061 (19)    | 0.0016 (19)     |
### Geometric parameters (Å, °)

| Bond          | Distance | Angle           | Torsion       |
|---------------|----------|-----------------|---------------|
| O1—C6         | 1.409 (3)| C13—H13B       | 0.9600        |
| O1—C17        | 1.356 (3)| C13—H13C       | 0.9600        |
| O2—C17        | 1.183 (3)| C14—H14        | 0.9800        |
| O3—C21        | 1.234 (3)| C14—C15        | 1.520 (4)     |
| O4—C21        | 1.264 (3)| C14—C16        | 1.510 (4)     |
| N1—C1         | 1.360 (4)| C15—H15A       | 0.9600        |
| N1—C2         | 1.359 (3)| C15—H15B       | 0.9600        |
| N1—H1         | 0.853 (10)| C15—H15C      | 0.9600        |
| N2—C10        | 1.505 (3)| C16—H16A       | 0.9600        |
| N2—C11        | 1.521 (4)| C16—H16B       | 0.9600        |
| N2—C14        | 1.517 (3)| C16—H16C       | 0.9600        |
| N2—H2         | 0.90 (3)| C17—C18        | 1.493 (3)     |
| C1—H1A        | 0.9300  | C18—H18A       | 0.9700        |
| C1—C8         | 1.359 (3)| C18—H18B       | 0.9700        |
| C2—C3         | 1.386 (4)| C18—C19        | 1.509 (3)     |
| C2—C7         | 1.420 (3)| C19—H19A       | 0.9700        |
| C3—H3         | 0.9300  | C19—H19B       | 0.9700        |
| C3—C4         | 1.370 (4)| C19—C20        | 1.498 (3)     |
| C4—H4         | 0.9300  | C20—H20A       | 0.9700        |
| C4—C5         | 1.400 (4)| C20—H20B       | 0.9700        |
| C5—H5         | 0.9300  | C20—C21        | 1.518 (4)     |
| C5—C6         | 1.358 (4)| O5—H5A         | 0.8200        |
| C6—C7         | 1.397 (3)| O5—C22         | 1.439 (8)     |
| C7—C8         | 1.427 (4)| C22—H22A       | 0.9700        |
| C8—C9         | 1.499 (3)| C22—H22B       | 0.9700        |
| C9—H9A        | 0.9700  | C22—C23        | 1.496 (8)     |
| C9—H9B        | 0.9700  | C23—H23A       | 0.9600        |
| C9—C10        | 1.521 (3)| C23—H23B       | 0.9600        |
| C10—H10A      | 0.9700  | C23—H23C       | 0.9600        |
| C10—H10B      | 0.9700  | O5A—H5AA       | 0.8200        |
| C11—H11       | 0.9800  | O5A—C22A       | 1.420 (8)     |
| C11—C12       | 1.517 (4)| C22A—H22C      | 0.9700        |
| C11—C13       | 1.514 (5)| C22A—H22D      | 0.9700        |
| C12—H12A      | 0.9600  | C22A—C23A      | 1.470 (8)     |
| C12—H12B      | 0.9600  | C23A—H23D      | 0.9600        |
| C12—H12C      | 0.9600  | C23A—H23E      | 0.9600        |
| C13—H13A      | 0.9600  | C23A—H23F      | 0.9600        |
| C17—O1—C6     | 116.79 (18)| C15—C14—H14   | 107.3         |
| C1—N1—H1      | 124 (2)  | C16—C14—N2     | 110.5 (2)     |
| C2—N1—C1      | 109.1 (2)| C16—C14—H14    | 107.3         |
| C2—N1—H1      | 127 (2)  | C16—C14—C15    | 112.3 (3)     |
| C10—N2—C11    | 111.28 (19)| C14—C15—H15A  | 109.5         |
| C10—N2—C14    | 112.0 (2)| C14—C15—H15B   | 109.5         |
| C10—N2—H2     | 106.1 (17)| C14—C15—H15C   | 109.5         |
| C11—N2—H2     | 107.4 (18)| H15A—C15—H15B | 109.5         |
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|-----------------------|-----------|-----------------------|-----------|
| C14—N2—C11           | 113.6 (2) | H15A—C15—H15C        | 109.5     |
| C14—N2—H2            | 106.0 (17)| H15B—C15—H15C        | 109.5     |
| N1—C1—H1A            | 124.5     | C14—C16—H16A         | 109.5     |
| C8—C1—N1             | 111.1 (3) | C14—C16—H16B         | 109.5     |
| C8—C1—H1A            | 124.5     | C14—C16—H16C         | 109.5     |
| N1—C2—C3             | 131.0 (2) | H16A—C16—H16B        | 109.5     |
| N1—C2—C7             | 106.9 (2) | H16A—C16—H16C        | 109.5     |
| C3—C2—C7             | 122.1 (2) | H16B—C16—H16C        | 109.5     |
| C2—C3—H3             | 120.9     | O1—C17—C18           | 111.0 (2) |
| C4—C3—C2             | 118.1 (2) | O2—C17—O1            | 122.7 (2) |
| C4—C3—H3             | 120.9     | O2—C17—C18           | 126.3 (2) |
| C3—C4—H4             | 119.3     | C17—C18—H18A         | 108.9     |
| C3—C4—C5             | 121.3 (3) | C17—C18—H18B         | 108.9     |
| C5—C4—H4             | 119.3     | C17—C18—C19          | 113.5 (2) |
| C4—C5—H5             | 120.0     | H18A—C18—H18B        | 107.7     |
| C6—C5—C4             | 120.0 (3) | C19—C18—H18A         | 108.9     |
| C6—C5—H5             | 120.0     | C19—C18—H18B         | 109.9     |
| C5—C6—O1             | 120.4 (2) | C18—C19—H19A         | 109.0     |
| C5—C6—C7             | 121.4 (2) | C18—C19—H19B         | 109.0     |
| C7—C6—O1             | 118.2 (2) | H19A—C19—H19B        | 107.8     |
| C7—C6—C8             | 107.4 (2) | C20—C19—C18          | 113.1 (2) |
| C6—C7—C2             | 117.0 (2) | C20—C19—H19A         | 109.0     |
| C6—C7—C8             | 135.6 (2) | C20—C19—H19B         | 109.0     |
| C1—C8—C7             | 105.6 (2) | C19—C20—H20A         | 108.4     |
| C1—C8—C9             | 124.9 (2) | C19—C20—H20B         | 108.4     |
| C7—C8—C9             | 128.8 (2) | C19—C20—C21          | 115.7 (2) |
| C8—C9—H9A            | 110.0     | H20A—C20—H20B        | 107.4     |
| C8—C9—H9B            | 110.0     | C21—C20—H20A         | 108.4     |
| C8—C9—C10            | 108.65 (19)| C21—C20—H20B        | 108.4     |
| H9A—C9—H9B           | 108.3     | O3—C21—O4            | 122.7 (2) |
| C10—C9—H9A           | 110.0     | O3—C21—C20           | 121.0 (2) |
| C10—C9—H9B           | 110.0     | O4—C21—C20           | 116.3 (2) |
| N2—C10—C9            | 114.35 (19)| C22—O5—H5A          | 109.5     |
| N2—C10—H10A          | 108.7     | O5—C22—H22A          | 110.0     |
| N2—C10—H10B          | 108.7     | O5—C22—H22B          | 110.0     |
| C9—C10—H10A          | 108.7     | O5—C22—C23           | 108.4 (8) |
| C9—C10—H10B          | 108.7     | H22A—C22—H22B        | 108.4     |
| H10A—C10—H10B        | 107.6     | C23—C22—H22A         | 110.0     |
| N2—C11—H11           | 108.1     | C23—C22—H22B         | 110.0     |
| C12—C11—N2           | 111.6 (2) | C22—C23—H23A         | 109.5     |
| C12—C11—H11          | 108.1     | C22—C23—H23B         | 109.5     |
| C13—C11—N2           | 110.0 (2) | C22—C23—H23C         | 109.5     |
| C13—C11—H11          | 108.1     | H23A—C23—H23B        | 109.5     |
| C13—C11—C12          | 111.0 (3) | H23A—C23—H23C        | 109.5     |
| C11—C12—H12A         | 109.5     | H23B—C23—H23C        | 109.5     |
| C11—C12—H12B         | 109.5     | C22A—O5A—H5AA        | 109.5     |
| C11—C12—H12C         | 109.5     | O5A—C22A—H22C        | 111.4     |
| H12A—C12—H12B        | 109.5     | O5A—C22A—H22D        | 111.4     |
H12A—C12—H12C 109.5 O5A—C22A—C23A 101.9 (7)
H12B—C12—H12C 109.5 H22C—C22A—H22D 109.3
C11—C13—H13A 109.5 C23A—C22A—H22C 111.4
C11—C13—H13B 109.5 C23A—C22A—H22D 111.4
C11—C13—H13C 109.5 C22A—C23A—H23D 109.5
H13A—C13—H13B 109.5 C22A—C23A—H23E 109.5
H13A—C13—H13C 109.5 C22A—C23A—H23F 109.5
H13B—C13—H13C 109.5 H23D—C23A—H23F 109.5
N2—C14—H14 107.3 H23D—C23A—H23F 109.5
N2—C14—C15 111.9 (2) H23E—C23A—H23F 109.5
O1—C6—C7—C2 179.04 (19) C6—O1—C17—O2 0.6 (4)
O1—C6—C7—C8 0.8 (4) C6—O1—C17—C18 −178.4 (2)
O1—C17—C18—C19 −176.7 (2) C6—C7—C8—C1 179.0 (3)
O2—C17—C18—C19 4.3 (5) C6—C7—C8—C9 8.9 (4)
N1—C1—C8—C7 0.0 (3) C7—C2—C3—C4 −0.1 (4)
N1—C1—C8—C9 170.6 (2) C7—C8—C9—C10 86.1 (3)
N1—C1—C8—C10 −178.3 (3) C8—C9—C10—N2 180.0 (2)
N1—C2—C7—C6 179.8 (2) C10—N2—C11—C12 −178.7 (3)
N1—C2—C7—C8 −1.1 (3) C10—N2—C11—C13 57.7 (3)
C1—C1—C8—C7 −177.5 (3) C10—N2—C14—C15 62.8 (3)
C1—C1—C8—C9 1.1 (3) C10—N2—C14—C16 −63.1 (3)
C1—C8—C9—C10 −82.3 (3) C11—N2—C10—C9 −105.4 (3)
C2—N1—C1—C8 0.7 (3) C11—N2—C14—C15 −64.3 (3)
C2—C3—C4—C5 1.0 (4) C11—N2—C14—C16 169.8 (2)
C2—C7—C8—C1 −0.7 (3) C14—N2—C10—C9 126.3 (2)
C2—C7—C8—C9 −169.4 (2) C14—N2—C11—C12 −51.2 (3)
C3—C2—C7—C6 177.7 (2) C14—N2—C11—C13 −174.8 (2)
C3—C2—C7—C8 −1.0 (3) C14—N2—C11—C13 87.0 (3)
C4—C5—C6—O1 −0.8 (4) C17—O1—C6—C5 95.2 (3)
C4—C5—C6—C7 −178.1 (2) C17—O1—C6—C7 176.7 (3)
C5—C6—C7—C2 −0.4 (4) C18—C19—C20—C21 172.6 (3)
C5—C6—C7—C8 1.2 (3) C19—C20—C21—O3 5.6 (5)
C2—C7—C8—C9 169.4 (2) C19—C20—C21—O4 −175.3 (3)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N2—H2···O4’ | 0.90 (3) | 1.79 (3) | 2.686 (3) | 177 (3) |
| N1—H1···O3u | 0.85 (1) | 1.91 (1) | 2.751 (3) | 167 (3) |
| O5—H5A···O4iii | 0.82 | 1.97 | 2.692 (10) | 147 |
| O5A—H5A···O4ii’ | 0.82 | 1.95 | 2.732 (6) | 160 |

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