



Psilacetin derivatives: fumarate salts of the methyl–ethyl, methyl–allyl and diallyl variants of the psilocin prodrug

Duyen N. K. Pham,^a Andrew R. Chadeayne,^b James A. Golen^a and David R. Manke^{a*}

Received 31 December 2020

Accepted 4 January 2021

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; tryptamines; indoles; fumarates; hydrogen bonding.

CCDC references: 2053845; 2053844; 2053843

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

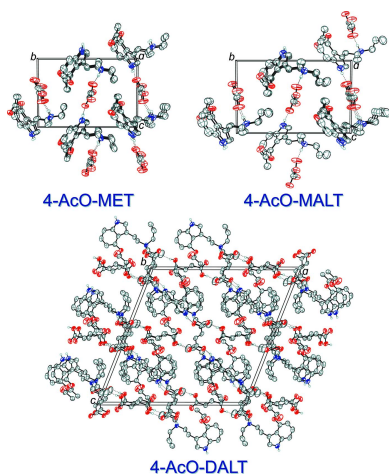
^aUniversity of Massachusetts Dartmouth, 285 Old Westport Road, North Dartmouth, MA 02747, USA, and ^bCaaMTech, Inc., 58 East Sunset Way, Suite 209, Issaquah, WA 98027, USA. *Correspondence e-mail: dmanke@umassd.edu

The solid-state structures of the salts of three psilacetin derivatives, namely, 4-acetoxy-*N*-ethyl-*N*-methyltryptammonium (4-AcO-MET) hydrofumarate {systematic name: [2-(4-acetyloxy-1*H*-indol-3-yl)ethyl](methyl)ethylazanium 3-carboxyprop-2-enoate}, C₁₅H₂₁N₂O₂⁺·C₄H₃O₄[−], 4-acetoxy-*N*-allyl-*N*-methyltryptammonium (4-AcO-MALT) hydrofumarate {systematic name: [2-(4-acetyloxy-1*H*-indol-3-yl)ethyl](methyl)prop-2-enylazanium 3-carboxyprop-2-enoate}, C₁₆H₂₁N₂O₂⁺·C₄H₃O₄[−], and 4-acetoxy-*N,N*-diallyltryptammonium (4-AcO-DALT) fumarate–fumaric acid (1/1) (systematic name: bis[[2-(4-acetyloxy-1*H*-indol-3-yl)ethyl]diprop-2-enylazanium} but-2-enedioate-(*E*)-butenedioic acid (1/1)), 2C₁₈H₂₃N₂O₂⁺·C₄H₂O₄^{2−}·C₄H₄O₄, are reported. All three salts possess a protonated tryptammonium cation. The 4-AcO-MET and 4-AcO-MALT compounds are charge-balanced by 3-carboxyacrylate (hydrofumarate) anions. The 4-AcO-DALT complex crystallizes as a two-to-one tryptammonium-to-fumarate salt, which co-crystallizes with a fumaric acid molecule. Each structure is consolidated by N–H···O and O–H···O hydrogen bonds.

1. Chemical context

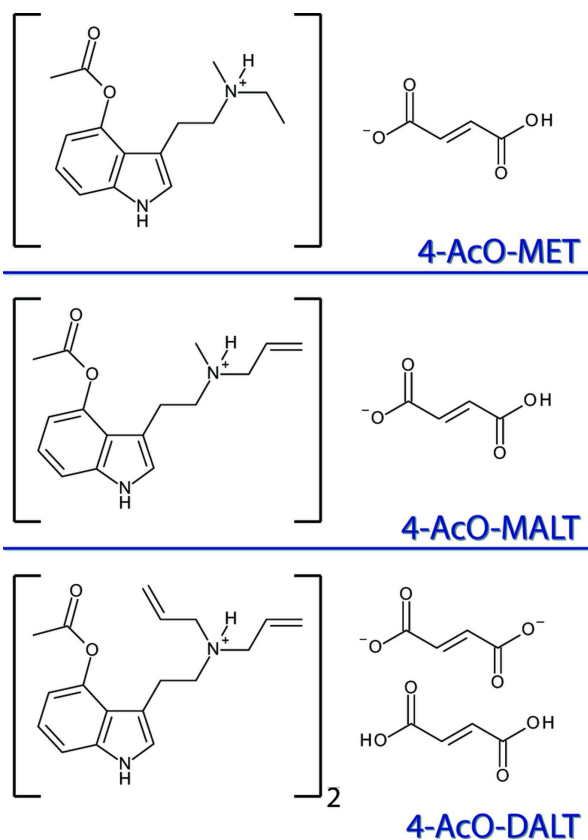
Psychotropic tryptamines have emerged as leading candidates in the treatment of mood disorders, including anxiety, addiction, depression and post-traumatic stress disorder (Byock, 2018; Daniel & Haberman, 2017). Perhaps the best known of these tryptamines is psilocybin, *N,N,N*-trimethyl-4-phosphoryloxytryptamine (C₁₂H₁₇N₂O₄P), which has recently been cleared for a number of clinical trials after receiving the ‘breakthrough therapy’ designation from the US Food and Drug Administration (Feltman, 2019). When psilocybin is consumed orally, it is hydrolysed to generate 4-hydroxy-*N,N*-dimethyltryptamine, C₁₂H₁₆N₂O (4-HO-DMT), or psilocin, which is the active metabolite. Psilocin is a potent serotonin 2a agonist, and is the primary origin of its psychoactive properties (Geiger *et al.*, 2018).

Psilacetin, 4-acetoxy-*N,N*-dimethyltryptamine, C₁₄H₁₈N₂O₂ (4-AcO-DMT), is a synthetic alternative to psilocybin. It also acts as a prodrug of psilocin, with the acetyl group of psilacetin being hydrolysed as it is metabolized, converting 4-AcO-DMT to 4-HO-DMT. Psilacetin is easier to synthesize than psilocybin, and can also be produced at a lower cost, making it, perhaps, a better candidate for the delivery of psilocin (Nichols & Frescas, 1999). Presumably, all 4-acetoxy-substituted tryptamines would similarly function as prodrugs for their active metabolite psilocin analogues. Three such



OPEN ACCESS

compounds are 4-acetoxy-*N*-ethyl-*N*-methyltryptamine, C₁₅H₂₀N₂O₂ (4-AcO-MET), 4-acetoxy-*N*-allyl-*N*-methyltryptamine, C₁₆H₂₀N₂O₂ (4-AcO-MALT), and 4-acetoxy-*N*,*N*-diallyltryptamine, C₁₈H₂₂N₂O₂ (4-AcO-DALT). These variations of psilocetin have garnered very little attention in the scientific literature, with only one reference made to 4-AcO-MET in a chromatographic screening article prior to this year (Lehmann *et al.*, 2017). A recent report on the activity of psilocetin analogues and their metabolites included 4-AcO-MET (Klein *et al.*, 2020). Herein, we report the first solid-state structures of the fumarate salts of 4-AcO-MET, 4-AcO-MALT and 4-AcO-DALT.



2. Structural commentary

The molecular structure of 4-AcO-MET hydrofumarate, (I), is shown in Fig. 1. The asymmetric unit contains one 4-acetoxy-*N*-ethyl-*N*-methyltryptammonium (C₁₅H₂₁N₂O₂⁺) cation and one hydrofumarate (C₄H₃O₄⁻) anion. The indole ring system of the cation is near planar with an r.m.s. deviation of 0.015 Å. The hydrofumarate anion is slightly twisted, demonstrating a deviation from planarity of 0.158 Å, and a C16/O3/O4 carboxylate to C19/O5/O6 carboxylic acid plane normal angle of 23.0 (3)°. The *N*-methyl-*N*-ethyl group of the cation is disordered over two orientations in a 0.76 (1):0.24 (7) ratio. The ethylammonium arm is turned slightly away from the plane of the indole, with C10–C9–C11–C12 and C10–C9–C11–C12A torsion angles of 39.7 (7) and 49.5 (2)°, respectively, for the two orientations.

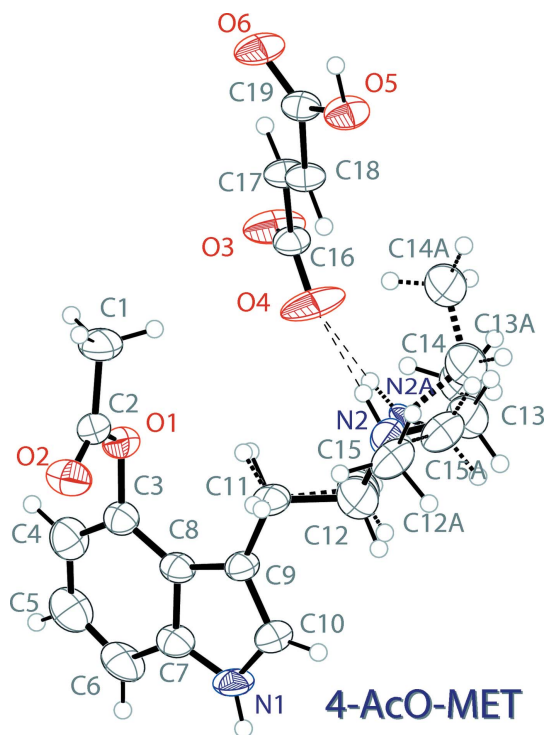


Figure 1
The molecular structure of 4-AcO-MET hydrofumarate (I), showing the atomic labeling. Displacement ellipsoids are drawn at the 50% probability level. Dashed bonds indicate a disordered component in the structures. Hydrogen bonds are shown as dashed lines.

The molecular structure of 4-AcO-MALT hydrofumarate, (II), is shown in Fig. 2. The asymmetric unit contains one

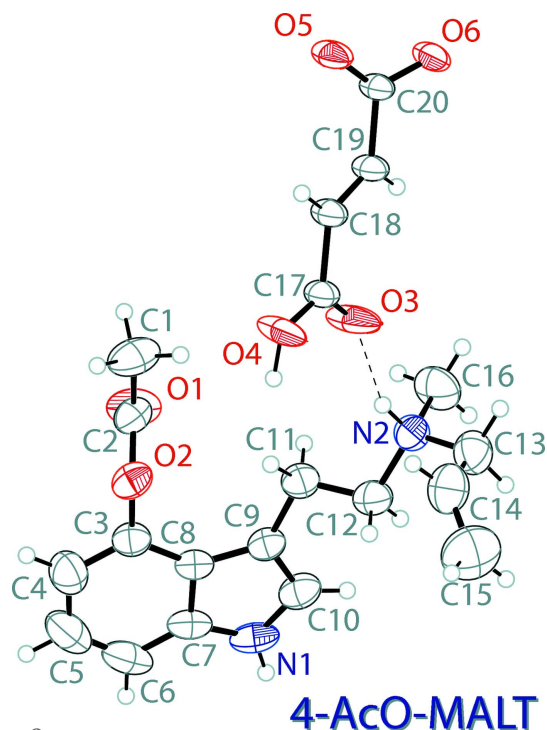


Figure 2
The molecular structure of 4-AcO-MALT hydrofumarate (II), showing the atomic labeling. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

4-acetoxy-*N*-allyl-*N*-methyltryptammonium ($C_{16}H_{21}N_2O_2^+$) cation and one hydrofumarate ($C_4H_3O_4^-$) anion. The indole ring system of the compound is almost planar with an r.m.s. deviation from planarity of 0.006 Å. The ethylammonium arm is turned slightly away from the plane of the indole ring, with a C10–C9–C11–C12 torsion angle of 39.8 (4)°. The hydrofumarate anion is slightly twisted, showing a deviation from planarity of 0.128 Å, and a C20/O5/O6 carboxylate to C17/O3/O4 carboxylic acid twist of 18.6 (2)°.

The molecular structure of 4-AcO-DALT fumarate–fumaric acid, (III), is shown in Fig. 3. The asymmetric unit contains one 4-acetoxy-*N,N*-diallyltryptammonium ($C_{18}H_{23}N_2O_2^+$) cation, one half of a fumarate ($C_2HO_2^-$) dianion, and one half of a fumaric acid ($C_2H_4O_2$) molecule. The indole ring system of the compound is near planar with a r.m.s. deviation from planarity of 0.016 Å. The ethylammonium arm is turned significantly away from the plane of the indole ring, with a C10–C9–C11–C12 torsion angle of 104.3 (2)°. The complete fumarate dianion is generated through crystallographic inversion symmetry, and is also near planar, with an r.m.s. deviation from planarity of 0.004 Å. The full disordered (*vide infra*) fumaric acid molecule is generated through inversion, and also demonstrates near planarity, with r.m.s. deviations from

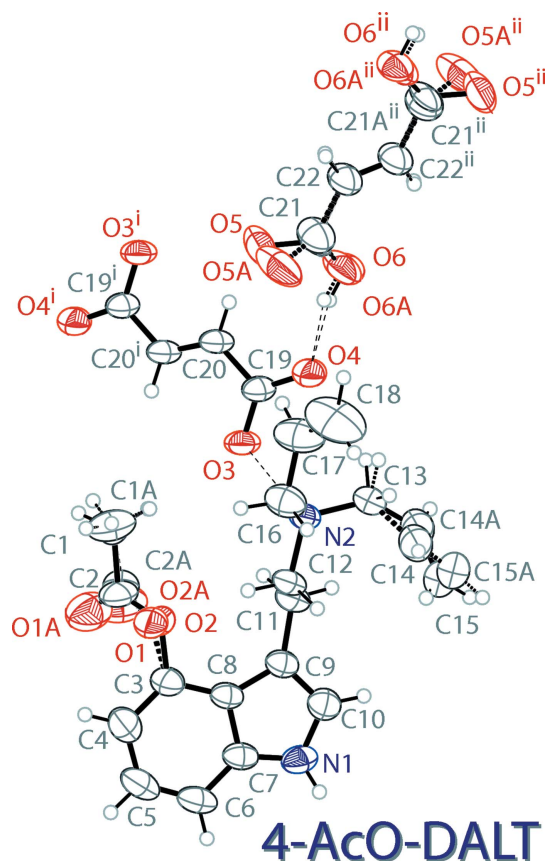


Figure 3

The molecular structure of 4-AcO-DALT fumarate fumaric acid (III), showing the atomic labeling. Displacement ellipsoids are drawn at the 50% probability level. Dashed bonds indicate a disordered component in the structures. Hydrogen bonds are shown as dashed lines. Symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$.

Table 1

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1 \cdots O6 ⁱ	0.86 (1)	2.02 (2)	2.858 (4)	165 (5)
N2–H2 \cdots O4	0.88 (2)	1.85 (4)	2.644 (6)	150 (7)
N2A–H2A \cdots O4	0.87 (2)	1.94 (6)	2.776 (14)	162 (17)
O5–H5A \cdots O3 ⁱⁱ	0.89 (2)	1.61 (2)	2.459 (4)	160 (6)

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

Table 2

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1 \cdots O5 ⁱ	0.87 (1)	2.00 (2)	2.857 (3)	169 (4)
O4–H4A \cdots O6 ⁱⁱ	0.89 (1)	1.56 (2)	2.454 (3)	175 (6)

Symmetry codes: (i) $x - 2, y, z - 1$; (ii) $x - 1, y, z$.

planarity of 0.082 and 0.083 Å for the two conformations. One of the allyl groups in the cation is disordered over two orientations with a 0.90 (1):0.10 (1) ratio. The fumaric acid molecule is also disordered over two components with a 0.52 (4):0.48 (4) ratio. The 4-acetoxy group also shows a disorder over two orientations with a 0.62 (4):0.38 (4) ratio. The carboxylate group of the fumarate anion is delocalized, with C–O distances of 1.251 (3) and 1.258 (2) Å.

3. Supramolecular features

In the extended structure of (I), the *N*-ethyl-*N*-methyltryptammonium cations and hydrofumarate anions are linked together in a two-dimensional network lying in the (010) plane through N–H \cdots O and O–H \cdots O hydrogen bonds (Table 1). The O–H group of the hydrofumarate hydrogen bonds with the carbonyl oxygen atom of the carboxylate unit of another hydrofumarate ion, the ammonium N–H hydrogen bonds to the negatively charged oxygen atom of the carboxylate group of a hydrofumarate ion, and the indole N–H hydrogen bonds to the carbonyl oxygen atom of the carboxylic acid unit of a hydrofumarate ion (Fig. 4, top). The packing of 4-AcO-MET hydrofumarate is shown at the top left of Fig. 5.

In the extended structure of (II), the *N*-allyl-*N*-methyltryptammonium cations and hydrofumarate anions are linked together in an infinite two-dimensional network parallel to (010) through N–H \cdots O and O–H \cdots O hydrogen bonds (Table 2). The O–H group of the hydrofumarate hydrogen bonds with the negatively charged oxygen atom of the carboxylate unit of another hydrofumarate ion, the indole N–H hydrogen bond to the carbonyl O atom of the carboxylate group of the hydrofumarate ion, and the ammonium N–H hydrogen bonds to the carbonyl oxygen atom of the carboxylic acid unit of the hydrofumarate ion (Fig. 4, center). The packing of 4-AcO-MALT hydrofumarate is shown at the top right of Fig. 5.

In the extended structure of (III), the *N,N*-diallyltryptammonium cations, fumarate dianions and fumaric acid molecules are linked together in a three-dimensional network through N–H \cdots O and O–H \cdots O hydrogen bonds (Table 3).

Table 3
Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1···O3 ⁱ	0.87 (1)	2.22 (2)	2.962 (2)	144 (2)
N2—H2···O3	0.88 (1)	1.87 (1)	2.7446 (19)	177 (2)
O6—H6A···O4	0.82	1.72	2.530 (17)	168
O6A—H6AA···O4	0.82	1.81	2.577 (16)	156

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

The O—H group of the fumaric acid, the ammonium N—H, and the indole N—H group all hydrogen bond to oxygen

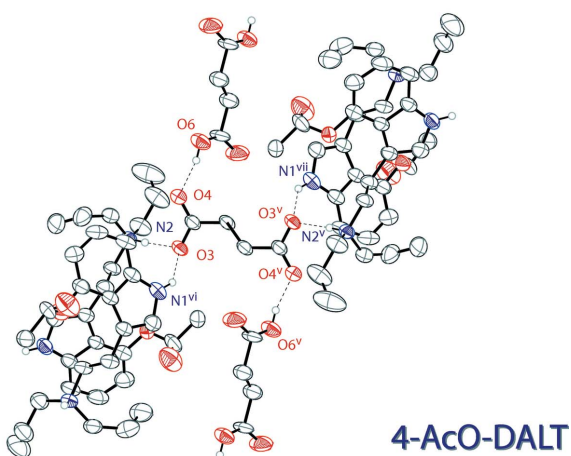
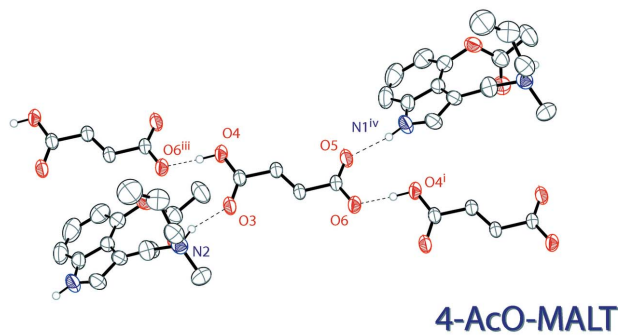
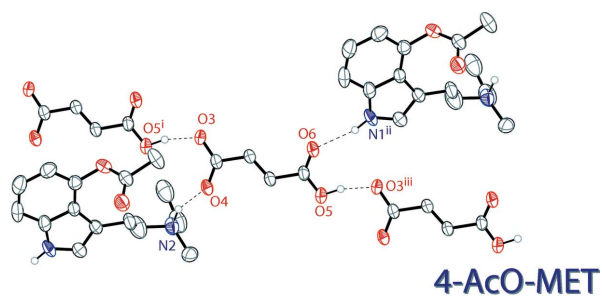


Figure 4
The hydrogen bonding environments of the hydrofumarate ion in the structure of (I) (top), the hydrofumarate ion in the structure of (II) (middle), and the fumarate dianion in the structure of (III) (bottom). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms not involved in hydrogen bonds are omitted for clarity. Only one component of disorders are shown. Symmetry codes: (i) $1 + x, y, z$; (ii) $-1 + x, y, 1 + z$; (iii) $-1 + x, y, z$; (iv) $2 + x, y, 1 + z$; (v) $1 - x, 2 - y, 1 - z$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$.

atoms of the fumarate dianion (Fig. 4, bottom). The packing of 4-AcO-DALT fumarate–fumaric acid is shown at the bottom of Fig. 5.

4. Database survey

The three structures reported here are closely related to psilacetin, which has been reported as both the hydrofumarate (HOCJUH: Chadeayne, Golen & Manke 2019b) and fumarate (XOFDOO: Chadeayne *et al.*, 2019a) salts. 4-AcO-MET and 4-AcO-MALT both form hydrofumarate salts, though the hydrogen-bonding networks vary from that observed for psilacetin. 4-AcO-DALT crystallizes as the fumarate salt, but also co-crystallizes with a fumaric acid molecule in the structure. The structure of the acetoxy-protected version of the active metabolite of aeruginascin, 4-acetoxy-*N,N,N*-trimethyltryptamine, has been reported (XUXDUS: Chadeayne, Pham, Reid *et al.*, 2020). The other reported structures of tryptammonium hydrofumarate monoanion salts are for 4-hydroxy-*N*-methyl-*N*-isopropyltryptamine and *N*-methyl-*N*-isopropyltryptamine (RONSUL and RONSOF: Chadeayne, Pham *et al.*, 2019b) and *N*-ethyl-*N*-*n*-propyltryptamine and

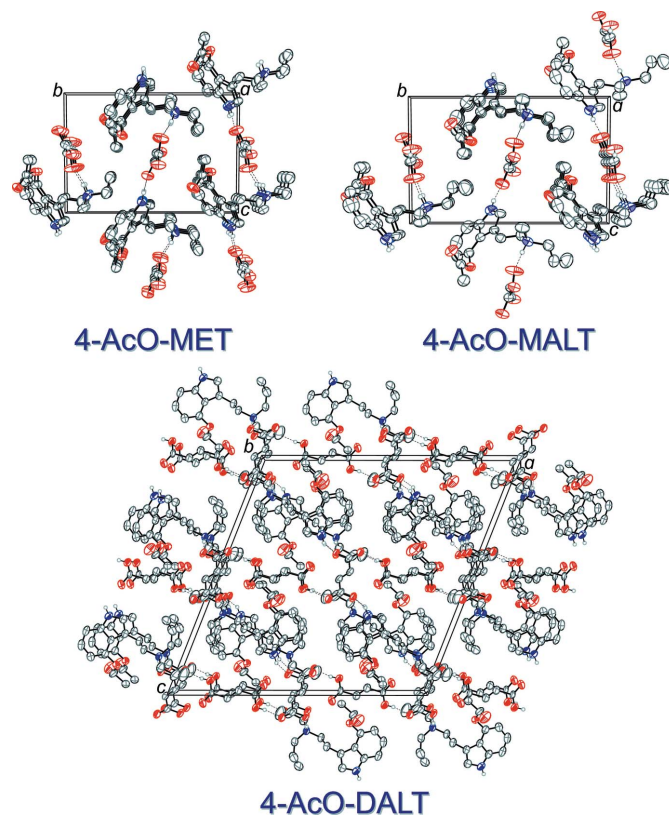


Figure 5
The crystal packing of (I) (top left), viewed along the *a*-axis direction, the crystal packing of (II) (top right), viewed along the *a*-axis direction and the crystal packing of (III) (bottom), viewed along the *b*-axis direction. The hydrogen bonds (Tables 1–3) are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms not involved in hydrogen bonds are omitted for clarity. Only one component of disorders are shown.

Table 4
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_{15}H_{21}N_2O_2^+ \cdot C_4H_3O_4^-$	$C_{16}H_{21}N_2O_2^+ \cdot C_4H_3O_4^-$	$2C_{18}H_{23}N_2O_2^+ \cdot C_4H_2O_4^{2-} \cdot C_4H_4O_4$
M_r	376.40	388.41	828.90
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1$	Monoclinic, $C2/c$
Temperature (K)	200	297	297
a, b, c (Å)	7.9555 (4), 13.3696 (7), 9.9708 (5)	7.9702 (4), 14.1788 (7), 9.8035 (5)	23.6642 (19), 8.4204 (7), 23.4002 (18)
β (°)	112.874 (2)	113.394 (2)	111.614 (2)
V (Å ³)	977.12 (9)	1016.80 (9)	4334.9 (6)
Z	2	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	0.10	0.09	0.09
Crystal size (mm)	0.24 × 0.2 × 0.2	0.34 × 0.24 × 0.2	0.22 × 0.2 × 0.12
Data collection			
Diffractometer	Bruker D8 Venture CMOS	Bruker D8 Venture CMOS	Bruker D8 Venture CMOS
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2018)	Multi-scan (<i>SADABS</i> ; Bruker, 2018)	Multi-scan (<i>SADABS</i> ; Bruker, 2018)
T_{\min} , T_{\max}	0.708, 0.745	0.686, 0.745	0.715, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21973, 3536, 3232	26393, 3797, 3516	99597, 4126, 3441
R_{int}	0.036	0.039	0.040
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.603	0.610	0.611
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.146, 1.04	0.043, 0.113, 1.04	0.051, 0.140, 1.06
No. of reflections	3536	3797	4126
No. of parameters	271	264	354
No. of restraints	15	4	114
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	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.39, -0.55	0.27, -0.16	0.50, -0.30
Absolute structure	Flack x determined using 1411 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)	Flack x determined using 1577 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)	–
Absolute structure parameter	-0.3 (3)	0.4 (3)	–

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *OLEX2* (Dolomanov *et al.*, 2009), and *publCIF* (Westrip, 2010).

N-allyl-*N*-methyltryptamine (CCDC 2012495 and CCDC 2012494: Chadeayne *et al.*, 2020c). The other reported structures of tryptammonium fumarate dianion salts are for 4-hydroxy-*N,N*-dipropyltryptamine (CCDC 1962339: Chadeayne *et al.*, 2019b), 4-hydroxy-*N*-methyl-*N*-isopropyltryptamine (CCDC 1987588: Chadeayne *et al.*, 2020a) and 4-hydroxy-*N*-methyltryptamine (CCDC 1992278: Chadeayne *et al.*, 2020b).

5. Synthesis and crystallization

Single crystals of 4-acetoxy-*N*-ethyl-*N*-methyltryptammonium hydrofumarate suitable for X-ray analysis were obtained from the slow evaporation of an ethanolic solution of a commercial sample (The Indole Shop). A commercial sample of 4-acetoxy-*N*-allyl-*N*-methyltryptammonium hydrofumarate (The Indole Shop) was recrystallized by the slow evaporation of an aqueous solution to yield samples suitable for single crystal X-ray diffraction studies. Single crystals of bis(4-acetoxy-*N,N*-diallyltryptammonium) fumarate fumaric acid suitable for X-ray analysis were obtained from the slow evaporation of an acetone solution of a commercial sample (The Indole Shop).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. O and N-bound H atoms were refined with the restraints O–H = 0.88 ± 1 and N–H = 0.87 ± 1 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{O})$. C-bound H atoms were positioned geometrically and refined using a riding model: C–H = 0.95 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C-methyl})$.

Acknowledgements

Financial statements and conflict of interest: This study was funded by CaaMTech, Inc. ARC reports an ownership interest in CaaMTech, Inc., which owns US and worldwide patent applications covering new tryptamine compounds, compositions, formulations, novel crystalline forms, and methods of making and using the same.

References

Bruker (2018). *APEX3*, *SAINT*, and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

- Byock, I. (2018). *J. Palliat. Med.* **21**, 417–421.
- Chadeayne, A. R., Golen, J. A. & Manke, D. R. (2019a). *Acta Cryst.* **E75**, 900–902.
- Chadeayne, A. R., Golen, J. A. & Manke, D. R. (2019b). *Psychedelic Science Review*. <https://psychedelicreview.com/the-crystal-structure-of-4-aco-dmt-fumarate/>.
- Chadeayne, A. R., Pham, D. N. K., Golen, J. A. & Manke, D. R. (2019). *IUCrData*, **4**, x190962.
- Chadeayne, A. R., Pham, D. N. K., Golen, J. A. & Manke, D. R. (2020a). *Acta Cryst.* **E76**, 514–517.
- Chadeayne, A. R., Pham, D. N. K., Golen, J. A. & Manke, D. R. (2020b). *Acta Cryst.* **E76**, 589–593.
- Chadeayne, A. R., Pham, D. N. K., Golen, J. A. & Manke, D. R. (2020c). *Acta Cryst.* **E76**, 1201–1205.
- Chadeayne, A. R., Pham, D. N. K., Reid, B. G., Golen, J. A. & Manke, D. R. (2020). *ACS Omega*, **5**, 16940–16943.
- Daniel, J. & Haberman, M. (2017). *Mental Health Clinician*, **7**, 24–28.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Feltman, R. (2019). *Popular Science*. <https://popsci.com/story/health/psilocybin-magic-mushroom-fda-breakthrough-depression/>
- Geiger, H. A., Wurst, M. G. & Daniels, R. N. (2018). *ACS Chem. Neurosci.* **9**, 2438–2447.
- Klein, A. K., Chatha, M., Laskowski, L. J., Anderson, E. I., Brandt, S. D., Chapman, S. J., McCorvy, J. D. & Halberstadt, A. L. (2020). *ACS Pharmacol. Transl. Sci.* **3**. <https://dx.doi.org/10.1021/acspsci.0c00176>
- Lehmann, S., Kieliba, T., Beike, J., Thevis, M. & Mercer-Chalmers-Bender, K. (2017). *J. Chromatogr. B*, **1064**, 124–138.
- Nichols, D. E. & Frescas, S. (1999). *Synthesis*, pp. 935–938.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2021). E77, 101-106 [https://doi.org/10.1107/S2056989021000116]

Psilacetin derivatives: fumarate salts of the methyl–ethyl, methyl–allyl and di-allyl variants of the psilocin prodrug

Duyen N. K. Pham, Andrew R. Chadeayne, James A. Golen and David R. Manke

Computing details

For all structures, data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINTE* (Bruker, 2018); data reduction: *SAINTE* (Bruker, 2018); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

[2-(4-Acetyloxy-1*H*-indol-3-yl)ethyl](methyl)ethylazanium 3-carboxyprop-2-enoate (I)

Crystal data

$C_{15}H_{21}N_2O_2^+ \cdot C_4H_3O_4^-$
 $M_r = 376.40$
 Monoclinic, $P2_1$
 $a = 7.9555$ (4) Å
 $b = 13.3696$ (7) Å
 $c = 9.9708$ (5) Å
 $\beta = 112.874$ (2)°
 $V = 977.12$ (9) Å³
 $Z = 2$

$F(000) = 400$
 $D_x = 1.279$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 9372 reflections
 $\theta = 2.7$ – 25.4 °
 $\mu = 0.10$ mm⁻¹
 $T = 200$ K
 Block, colorless
 0.24 × 0.2 × 0.2 mm

Data collection

Bruker D8 Venture CMOS
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2018)
 $T_{\min} = 0.708$, $T_{\max} = 0.745$
 21973 measured reflections

3536 independent reflections
 3232 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 25.4$ °, $\theta_{\min} = 2.8$ °
 $h = -9 \rightarrow 9$
 $k = -16 \rightarrow 16$
 $l = -11 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.146$
 $S = 1.04$
 3536 reflections
 271 parameters
 15 restraints
 Hydrogen site location: mixed

H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0859P)^2 + 0.4056P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.39$ e Å⁻³
 $\Delta\rho_{\min} = -0.55$ e Å⁻³
 Absolute structure: Flack x determined using
 1411 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
 Absolute structure parameter: -0.3 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.8969 (4)	0.6685 (2)	0.3476 (3)	0.0419 (7)	
O2	0.6590 (4)	0.7649 (2)	0.2143 (3)	0.0527 (8)	
O3	0.6091 (4)	0.4634 (4)	0.5977 (3)	0.0643 (11)	
O4	0.3948 (4)	0.4494 (4)	0.3791 (3)	0.0726 (12)	
O5	-0.1636 (4)	0.4458 (3)	0.4883 (3)	0.0464 (7)	
H5A	-0.228 (7)	0.461 (5)	0.541 (5)	0.070*	
O6	0.0341 (4)	0.5232 (3)	0.6851 (3)	0.0530 (8)	
N1	0.8829 (5)	0.5556 (3)	-0.1012 (4)	0.0445 (8)	
H1	0.909 (7)	0.546 (4)	-0.177 (3)	0.053*	
C1	0.6770 (8)	0.7029 (4)	0.4462 (5)	0.0609 (13)	
H1A	0.771261	0.727703	0.536780	0.091*	
H1B	0.656163	0.631605	0.456386	0.091*	
H1C	0.563452	0.739969	0.425935	0.091*	
C2	0.7388 (6)	0.7176 (3)	0.3229 (4)	0.0398 (9)	
C3	0.9685 (5)	0.6723 (3)	0.2378 (4)	0.0377 (9)	
C4	1.1178 (6)	0.7317 (3)	0.2611 (5)	0.0505 (11)	
H4	1.165836	0.772222	0.345887	0.061*	
C5	1.1983 (7)	0.7322 (4)	0.1596 (6)	0.0581 (13)	
H5	1.303718	0.772121	0.177668	0.070*	
C6	1.1292 (7)	0.6765 (4)	0.0340 (6)	0.0547 (12)	
H6	1.183090	0.678752	-0.035920	0.066*	
C7	0.9784 (6)	0.6171 (3)	0.0127 (5)	0.0399 (9)	
C8	0.8952 (5)	0.6117 (3)	0.1155 (4)	0.0344 (8)	
C9	0.7462 (5)	0.5416 (3)	0.0580 (4)	0.0347 (8)	
C10	0.7465 (6)	0.5098 (3)	-0.0720 (4)	0.0413 (9)	
H10	0.663545	0.462369	-0.133842	0.050*	
C11	0.6170 (6)	0.5075 (3)	0.1251 (5)	0.0462 (10)	
H11A	0.500209	0.544176	0.080710	0.055*	0.760 (7)
H11B	0.669365	0.522179	0.230754	0.055*	0.760 (7)
H11C	0.493724	0.534844	0.069534	0.055*	0.240 (7)
H11D	0.658515	0.532211	0.226482	0.055*	0.240 (7)
N2	0.4319 (8)	0.3670 (4)	0.1512 (6)	0.0478 (14)	0.760 (7)
H2	0.460 (10)	0.389 (6)	0.240 (4)	0.057*	0.760 (7)
C12	0.583 (2)	0.3971 (6)	0.1019 (15)	0.0747 (14)	0.760 (7)
H12A	0.695565	0.359695	0.158198	0.090*	0.760 (7)
H12B	0.546626	0.380879	-0.002452	0.090*	0.760 (7)
C13	0.4415 (12)	0.2578 (5)	0.1741 (9)	0.0747 (14)	0.760 (7)
H13A	0.434068	0.222514	0.084645	0.090*	0.760 (7)
H13B	0.339870	0.234739	0.200220	0.090*	0.760 (7)

C14	0.6257 (12)	0.2371 (6)	0.2991 (9)	0.0747 (14)	0.760 (7)
H14A	0.609720	0.186452	0.364171	0.112*	0.760 (7)
H14B	0.671948	0.299017	0.353700	0.112*	0.760 (7)
H14C	0.712937	0.212798	0.259233	0.112*	0.760 (7)
C15	0.2372 (8)	0.3878 (5)	0.0459 (7)	0.0518 (14)	0.760 (7)
H15A	0.222136	0.459583	0.024871	0.078*	0.760 (7)
H15B	0.152161	0.366435	0.089854	0.078*	0.760 (7)
H15C	0.211710	0.350719	-0.044649	0.078*	0.760 (7)
N2A	0.5331 (17)	0.3315 (9)	0.2166 (13)	0.024 (3)	0.240 (7)
H2A	0.51 (2)	0.371 (11)	0.278 (13)	0.029*	0.240 (7)
C12A	0.609 (7)	0.3915 (11)	0.124 (5)	0.0747 (14)	0.240 (7)
H12C	0.539526	0.371383	0.021726	0.090*	0.240 (7)
H12D	0.736058	0.367924	0.149239	0.090*	0.240 (7)
C13A	0.555 (4)	0.2363 (15)	0.305 (2)	0.0747 (14)	0.240 (7)
H13C	0.640638	0.192254	0.282152	0.090*	0.240 (7)
H13D	0.435712	0.202054	0.269481	0.090*	0.240 (7)
C14A	0.623 (4)	0.242 (2)	0.471 (2)	0.0747 (14)	0.240 (7)
H14D	0.724365	0.195394	0.515462	0.112*	0.240 (7)
H14E	0.523313	0.224946	0.501539	0.112*	0.240 (7)
H14F	0.664930	0.310475	0.503391	0.112*	0.240 (7)
C15A	0.335 (2)	0.3065 (18)	0.116 (2)	0.0518 (14)	0.240 (7)
H15D	0.277454	0.268541	0.170713	0.078*	0.240 (7)
H15E	0.334919	0.266491	0.033717	0.078*	0.240 (7)
H15F	0.267400	0.368689	0.079997	0.078*	0.240 (7)
C16	0.4441 (5)	0.4620 (3)	0.5089 (4)	0.0363 (8)	
C17	0.3065 (5)	0.4772 (3)	0.5751 (4)	0.0384 (9)	
H17	0.348389	0.491198	0.676267	0.046*	
C18	0.1302 (5)	0.4720 (3)	0.4987 (4)	0.0375 (8)	
H18	0.087892	0.460653	0.396827	0.045*	
C19	-0.0063 (5)	0.4833 (3)	0.5668 (4)	0.0366 (9)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0513 (17)	0.0443 (15)	0.0315 (13)	0.0013 (13)	0.0174 (12)	-0.0005 (12)
O2	0.0541 (18)	0.060 (2)	0.0505 (18)	0.0116 (16)	0.0277 (15)	0.0128 (16)
O3	0.0266 (14)	0.130 (3)	0.0416 (16)	0.0008 (18)	0.0187 (12)	-0.0061 (19)
O4	0.0403 (16)	0.144 (4)	0.0440 (18)	0.002 (2)	0.0277 (14)	-0.027 (2)
O5	0.0324 (14)	0.069 (2)	0.0456 (16)	-0.0014 (13)	0.0234 (12)	-0.0050 (14)
O6	0.0393 (15)	0.087 (2)	0.0433 (16)	-0.0022 (15)	0.0274 (13)	-0.0111 (16)
N1	0.057 (2)	0.051 (2)	0.0400 (18)	0.0093 (17)	0.0352 (17)	0.0022 (15)
C1	0.089 (4)	0.057 (3)	0.059 (3)	0.012 (3)	0.054 (3)	0.006 (2)
C2	0.052 (2)	0.036 (2)	0.039 (2)	-0.0023 (17)	0.0260 (18)	-0.0033 (17)
C3	0.038 (2)	0.0386 (19)	0.039 (2)	0.0028 (16)	0.0168 (17)	0.0023 (16)
C4	0.043 (2)	0.051 (3)	0.051 (2)	-0.0071 (19)	0.0112 (19)	0.000 (2)
C5	0.043 (2)	0.063 (3)	0.073 (3)	-0.009 (2)	0.028 (2)	0.005 (3)
C6	0.049 (3)	0.056 (3)	0.077 (3)	0.003 (2)	0.045 (2)	0.012 (2)
C7	0.040 (2)	0.042 (2)	0.046 (2)	0.0097 (17)	0.0263 (18)	0.0063 (17)

C8	0.0338 (19)	0.0388 (19)	0.0367 (19)	0.0029 (15)	0.0201 (16)	0.0036 (15)
C9	0.0394 (19)	0.0374 (19)	0.0324 (18)	0.0029 (15)	0.0194 (16)	-0.0015 (15)
C10	0.045 (2)	0.047 (2)	0.0367 (19)	0.0011 (18)	0.0205 (17)	-0.0045 (17)
C11	0.052 (2)	0.053 (2)	0.048 (2)	-0.0120 (19)	0.035 (2)	-0.0122 (19)
N2	0.055 (3)	0.046 (3)	0.054 (3)	-0.016 (3)	0.034 (3)	-0.018 (3)
C12	0.100 (4)	0.061 (2)	0.084 (3)	-0.020 (2)	0.060 (3)	-0.009 (2)
C13	0.100 (4)	0.061 (2)	0.084 (3)	-0.020 (2)	0.060 (3)	-0.009 (2)
C14	0.100 (4)	0.061 (2)	0.084 (3)	-0.020 (2)	0.060 (3)	-0.009 (2)
C15	0.043 (3)	0.064 (4)	0.046 (3)	0.000 (3)	0.014 (2)	-0.016 (3)
N2A	0.024 (6)	0.025 (6)	0.021 (6)	-0.009 (5)	0.007 (5)	0.004 (5)
C12A	0.100 (4)	0.061 (2)	0.084 (3)	-0.020 (2)	0.060 (3)	-0.009 (2)
C13A	0.100 (4)	0.061 (2)	0.084 (3)	-0.020 (2)	0.060 (3)	-0.009 (2)
C14A	0.100 (4)	0.061 (2)	0.084 (3)	-0.020 (2)	0.060 (3)	-0.009 (2)
C15A	0.043 (3)	0.064 (4)	0.046 (3)	0.000 (3)	0.014 (2)	-0.016 (3)
C16	0.0355 (18)	0.045 (2)	0.0360 (19)	-0.0002 (17)	0.0220 (15)	-0.0020 (16)
C17	0.0327 (18)	0.056 (2)	0.0319 (17)	0.0024 (17)	0.0184 (15)	0.0001 (17)
C18	0.0340 (18)	0.051 (2)	0.0343 (18)	0.0040 (17)	0.0209 (15)	0.0009 (17)
C19	0.0316 (18)	0.048 (2)	0.0373 (19)	0.0052 (16)	0.0209 (15)	0.0039 (17)

Geometric parameters (Å, °)

O1—C2	1.354 (5)	N2—C12	1.517 (10)
O1—C3	1.418 (5)	N2—C13	1.476 (8)
O2—C2	1.200 (5)	N2—C15	1.521 (8)
O3—C16	1.267 (5)	C12—H12A	0.9900
O4—C16	1.209 (5)	C12—H12B	0.9900
O5—H5A	0.886 (15)	C13—H13A	0.9900
O5—C19	1.292 (5)	C13—H13B	0.9900
O6—C19	1.218 (5)	C13—C14	1.535 (10)
N1—H1	0.862 (14)	C14—H14A	0.9800
N1—C7	1.368 (6)	C14—H14B	0.9800
N1—C10	1.372 (6)	C14—H14C	0.9800
C1—H1A	0.9800	C15—H15A	0.9800
C1—H1B	0.9800	C15—H15B	0.9800
C1—H1C	0.9800	C15—H15C	0.9800
C1—C2	1.504 (6)	N2A—H2A	0.870 (15)
C3—C4	1.371 (6)	N2A—C12A	1.518 (14)
C3—C8	1.390 (6)	N2A—C13A	1.521 (13)
C4—H4	0.9500	N2A—C15A	1.538 (12)
C4—C5	1.392 (7)	C12A—H12C	0.9900
C5—H5	0.9500	C12A—H12D	0.9900
C5—C6	1.376 (8)	C13A—H13C	0.9900
C6—H6	0.9500	C13A—H13D	0.9900
C6—C7	1.385 (7)	C13A—C14A	1.532 (14)
C7—C8	1.422 (5)	C14A—H14D	0.9800
C8—C9	1.443 (6)	C14A—H14E	0.9800
C9—C10	1.365 (5)	C14A—H14F	0.9800
C9—C11	1.500 (5)	C15A—H15D	0.9800

C10—H10	0.9500	C15A—H15E	0.9800
C11—H11A	0.9900	C15A—H15F	0.9800
C11—H11B	0.9900	C16—C17	1.495 (5)
C11—H11C	0.9900	C17—H17	0.9500
C11—H11D	0.9900	C17—C18	1.312 (5)
C11—C12	1.501 (9)	C18—H18	0.9500
C11—C12A	1.551 (14)	C18—C19	1.496 (5)
N2—H2	0.875 (15)		
C2—O1—C3	117.8 (3)	H12A—C12—H12B	108.3
C19—O5—H5A	101 (4)	N2—C13—H13A	110.5
C7—N1—H1	125 (3)	N2—C13—H13B	110.5
C7—N1—C10	108.7 (3)	N2—C13—C14	106.2 (6)
C10—N1—H1	126 (3)	H13A—C13—H13B	108.7
H1A—C1—H1B	109.5	C14—C13—H13A	110.5
H1A—C1—H1C	109.5	C14—C13—H13B	110.5
H1B—C1—H1C	109.5	C13—C14—H14A	109.5
C2—C1—H1A	109.5	C13—C14—H14B	109.5
C2—C1—H1B	109.5	C13—C14—H14C	109.5
C2—C1—H1C	109.5	H14A—C14—H14B	109.5
O1—C2—C1	111.3 (4)	H14A—C14—H14C	109.5
O2—C2—O1	123.2 (4)	H14B—C14—H14C	109.5
O2—C2—C1	125.4 (4)	N2—C15—H15A	109.5
C4—C3—O1	118.1 (4)	N2—C15—H15B	109.5
C4—C3—C8	121.8 (4)	N2—C15—H15C	109.5
C8—C3—O1	119.9 (3)	H15A—C15—H15B	109.5
C3—C4—H4	120.2	H15A—C15—H15C	109.5
C3—C4—C5	119.5 (4)	H15B—C15—H15C	109.5
C5—C4—H4	120.2	C12A—N2A—H2A	109 (10)
C4—C5—H5	119.2	C12A—N2A—C13A	144 (2)
C6—C5—C4	121.7 (4)	C12A—N2A—C15A	106 (2)
C6—C5—H5	119.2	C13A—N2A—H2A	97 (10)
C5—C6—H6	121.1	C13A—N2A—C15A	93.2 (16)
C5—C6—C7	117.8 (4)	C15A—N2A—H2A	101 (10)
C7—C6—H6	121.1	C11—C12A—H12C	106.5
N1—C7—C6	129.8 (4)	C11—C12A—H12D	106.5
N1—C7—C8	107.7 (3)	N2A—C12A—C11	123.2 (16)
C6—C7—C8	122.5 (4)	N2A—C12A—H12C	106.5
C3—C8—C7	116.7 (4)	N2A—C12A—H12D	106.5
C3—C8—C9	136.6 (4)	H12C—C12A—H12D	106.5
C7—C8—C9	106.7 (3)	N2A—C13A—H13C	107.4
C8—C9—C11	128.3 (3)	N2A—C13A—H13D	107.4
C10—C9—C8	105.9 (3)	N2A—C13A—C14A	119.8 (18)
C10—C9—C11	125.7 (4)	H13C—C13A—H13D	106.9
N1—C10—H10	124.6	C14A—C13A—H13C	107.4
C9—C10—N1	110.9 (4)	C14A—C13A—H13D	107.4
C9—C10—H10	124.6	C13A—C14A—H14D	109.5
C9—C11—H11A	109.6	C13A—C14A—H14E	109.5

C9—C11—H11B	109.6	C13A—C14A—H14F	109.5
C9—C11—H11C	109.8	H14D—C14A—H14E	109.5
C9—C11—H11D	109.8	H14D—C14A—H14F	109.5
C9—C11—C12	110.2 (5)	H14E—C14A—H14F	109.5
C9—C11—C12A	109.4 (10)	N2A—C15A—H15D	109.5
H11A—C11—H11B	108.1	N2A—C15A—H15E	109.5
H11C—C11—H11D	108.2	N2A—C15A—H15F	109.5
C12—C11—H11A	109.6	H15D—C15A—H15E	109.5
C12—C11—H11B	109.6	H15D—C15A—H15F	109.5
C12A—C11—H11C	109.8	H15E—C15A—H15F	109.5
C12A—C11—H11D	109.8	O3—C16—C17	115.3 (3)
C12—N2—H2	108 (6)	O4—C16—O3	124.5 (3)
C12—N2—C15	116.7 (8)	O4—C16—C17	120.2 (3)
C13—N2—H2	101 (6)	C16—C17—H17	118.7
C13—N2—C12	108.3 (6)	C18—C17—C16	122.5 (3)
C13—N2—C15	105.4 (5)	C18—C17—H17	118.7
C15—N2—H2	115 (5)	C17—C18—H18	118.9
C11—C12—N2	109.3 (6)	C17—C18—C19	122.2 (3)
C11—C12—H12A	109.8	C19—C18—H18	118.9
C11—C12—H12B	109.8	O5—C19—C18	112.9 (3)
N2—C12—H12A	109.8	O6—C19—O5	125.9 (3)
N2—C12—H12B	109.8	O6—C19—C18	121.2 (3)
O1—C3—C4—C5	176.0 (4)	C7—C8—C9—C11	178.7 (4)
O1—C3—C8—C7	-177.9 (3)	C8—C3—C4—C5	0.4 (6)
O1—C3—C8—C9	3.9 (7)	C8—C9—C10—N1	-0.8 (5)
O3—C16—C17—C18	-175.9 (4)	C8—C9—C11—C12	-139.1 (7)
O4—C16—C17—C18	3.9 (7)	C8—C9—C11—C12A	-129 (2)
N1—C7—C8—C3	-177.6 (3)	C9—C11—C12—N2	-172.0 (7)
N1—C7—C8—C9	1.1 (4)	C9—C11—C12A—N2A	164 (3)
C2—O1—C3—C4	105.8 (4)	C10—N1—C7—C6	178.4 (4)
C2—O1—C3—C8	-78.5 (5)	C10—N1—C7—C8	-1.6 (5)
C3—O1—C2—O2	-1.2 (6)	C10—C9—C11—C12	39.6 (9)
C3—O1—C2—C1	177.7 (4)	C10—C9—C11—C12A	49 (2)
C3—C4—C5—C6	1.8 (7)	C11—C9—C10—N1	-179.8 (4)
C3—C8—C9—C10	178.2 (5)	C12—N2—C13—C14	63.8 (9)
C3—C8—C9—C11	-2.9 (7)	C13—N2—C12—C11	-161.4 (8)
C4—C3—C8—C7	-2.3 (6)	C15—N2—C12—C11	80.0 (10)
C4—C3—C8—C9	179.4 (4)	C15—N2—C13—C14	-170.6 (5)
C4—C5—C6—C7	-1.7 (8)	C12A—N2A—C13A—C14A	110 (4)
C5—C6—C7—N1	179.6 (4)	C13A—N2A—C12A—C11	-144 (3)
C5—C6—C7—C8	-0.4 (7)	C15A—N2A—C12A—C11	97 (4)
C6—C7—C8—C3	2.4 (6)	C15A—N2A—C13A—C14A	-128 (2)
C6—C7—C8—C9	-178.9 (4)	C16—C17—C18—C19	177.5 (4)
C7—N1—C10—C9	1.6 (5)	C17—C18—C19—O5	-159.5 (4)
C7—C8—C9—C10	-0.2 (4)	C17—C18—C19—O6	19.7 (6)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O6 ⁱ	0.86 (1)	2.02 (2)	2.858 (4)	165 (5)
N2—H2 \cdots O4	0.88 (2)	1.85 (4)	2.644 (6)	150 (7)
N2 <i>A</i> —H2 <i>A</i> \cdots O4	0.87 (2)	1.94 (6)	2.776 (14)	162 (17)
O5—H5 <i>A</i> \cdots O3 ⁱⁱ	0.89 (2)	1.61 (2)	2.459 (4)	160 (6)

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

[2-(4-Acetyloxy-1*H*-indol-3-yl)ethyl](methyl)prop-2-enylazanium 3-carboxyprop-2-enoate (II)

Crystal data

$C_{16}H_{21}N_2O_2^+ \cdot C_4H_3O_4^-$

$M_r = 388.41$

Monoclinic, $P2_1$

$a = 7.9702$ (4) Å

$b = 14.1788$ (7) Å

$c = 9.8035$ (5) Å

$\beta = 113.394$ (2)°

$V = 1016.80$ (9) Å³

$Z = 2$

$F(000) = 412$

$D_x = 1.269$ Mg m⁻³

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

Cell parameters from 9882 reflections

$\theta = 2.7$ – 25.6 °

$\mu = 0.09$ mm⁻¹

$T = 297$ K

BLOCK, colourless

$0.34 \times 0.24 \times 0.2$ mm

Data collection

Bruker D8 Venture CMOS

diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2018)

$T_{\min} = 0.686$, $T_{\max} = 0.745$

26393 measured reflections

3797 independent reflections

3516 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 25.7$ °, $\theta_{\min} = 2.8$ °

$h = -9 \rightarrow 9$

$k = -17 \rightarrow 17$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.113$

$S = 1.04$

3797 reflections

264 parameters

4 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0592P)^2 + 0.2448P]$

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

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

$\Delta\rho_{\max} = 0.27$ e Å⁻³

$\Delta\rho_{\min} = -0.16$ e Å⁻³

Absolute structure: Flack x determined using

1577 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: 0.4 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.0798 (3)	0.7896 (2)	0.2116 (3)	0.0688 (8)
O2	-0.0241 (3)	0.69624 (16)	0.3445 (2)	0.0496 (5)
O3	0.5149 (3)	0.4747 (3)	0.3619 (3)	0.0834 (11)
O4	0.5188 (3)	0.4841 (3)	0.5856 (3)	0.0701 (8)
H4A	0.397 (2)	0.484 (4)	0.543 (5)	0.105*
O5	1.1781 (3)	0.53485 (19)	0.6822 (2)	0.0559 (6)
O6	1.1837 (2)	0.47635 (18)	0.4735 (2)	0.0493 (5)
N1	-0.4734 (4)	0.5921 (2)	-0.1031 (3)	0.0585 (8)
H1	-0.577 (3)	0.580 (3)	-0.176 (3)	0.070*
N2	0.2259 (4)	0.4086 (2)	0.1361 (3)	0.0499 (6)
H2	0.297 (4)	0.436 (3)	0.221 (3)	0.060*
C1	0.2902 (5)	0.7280 (3)	0.4444 (5)	0.0754 (12)
H1A	0.377223	0.771990	0.436158	0.113*
H1B	0.330726	0.664822	0.439678	0.113*
H1C	0.279217	0.737271	0.537570	0.113*
C2	0.1079 (5)	0.7436 (2)	0.3193 (4)	0.0506 (8)
C3	-0.2038 (4)	0.7039 (2)	0.2363 (3)	0.0464 (7)
C4	-0.3218 (6)	0.7650 (3)	0.2617 (5)	0.0642 (9)
H4	-0.281087	0.803090	0.345811	0.077*
C5	-0.5046 (6)	0.7694 (3)	0.1595 (6)	0.0776 (12)
H5	-0.584090	0.810842	0.177293	0.093*
C6	-0.5689 (5)	0.7147 (3)	0.0352 (5)	0.0685 (11)
H6	-0.690394	0.718337	-0.031497	0.082*
C7	-0.4473 (4)	0.6531 (2)	0.0109 (4)	0.0494 (8)
C8	-0.2618 (4)	0.6455 (2)	0.1114 (3)	0.0401 (6)
C9	-0.1793 (4)	0.5762 (2)	0.0515 (3)	0.0418 (6)
C10	-0.3140 (5)	0.5459 (3)	-0.0778 (3)	0.0531 (8)
H10	-0.299037	0.500150	-0.139982	0.064*
C11	0.0171 (4)	0.5439 (2)	0.1121 (4)	0.0491 (7)
H11A	0.082400	0.578146	0.062769	0.059*
H11B	0.074142	0.558138	0.217389	0.059*
C12	0.0315 (4)	0.4409 (2)	0.0897 (4)	0.0554 (8)
H12A	-0.036085	0.425881	-0.014403	0.066*
H12B	-0.024264	0.406630	0.146635	0.066*
C13	0.2451 (6)	0.3047 (3)	0.1669 (5)	0.0656 (10)
H13A	0.165728	0.271014	0.078805	0.079*
H13B	0.369974	0.285978	0.188000	0.079*
C14	0.1994 (6)	0.2777 (3)	0.2918 (5)	0.0745 (11)
H14	0.260747	0.308976	0.381312	0.089*
C15	0.0818 (9)	0.2144 (4)	0.2897 (8)	0.1105 (19)
H15A	0.017104	0.181308	0.202624	0.133*
H15B	0.061757	0.201983	0.375131	0.133*
C16	0.3019 (6)	0.4354 (4)	0.0257 (4)	0.0741 (12)
H16A	0.425726	0.413518	0.058781	0.111*
H16B	0.299241	0.502755	0.015387	0.111*

H16C	0.229752	0.407199	-0.068548	0.111*
C17	0.5946 (3)	0.4843 (2)	0.4951 (3)	0.0412 (6)
C18	0.7971 (3)	0.4950 (2)	0.5624 (3)	0.0418 (6)
H18	0.853754	0.504450	0.664454	0.050*
C19	0.8996 (3)	0.4919 (2)	0.4870 (3)	0.0406 (6)
H19	0.844150	0.482380	0.384840	0.049*
C20	1.1021 (3)	0.5030 (2)	0.5574 (3)	0.0372 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0517 (14)	0.0828 (19)	0.0643 (16)	-0.0064 (13)	0.0149 (12)	0.0250 (14)
O2	0.0521 (12)	0.0543 (12)	0.0358 (10)	-0.0098 (10)	0.0102 (9)	-0.0002 (9)
O3	0.0276 (10)	0.176 (3)	0.0441 (13)	-0.0232 (16)	0.0119 (9)	-0.0257 (17)
O4	0.0255 (10)	0.142 (3)	0.0462 (12)	-0.0035 (14)	0.0177 (9)	-0.0141 (15)
O5	0.0243 (9)	0.0955 (18)	0.0443 (12)	-0.0058 (10)	0.0098 (9)	-0.0179 (11)
O6	0.0274 (9)	0.0772 (15)	0.0464 (11)	-0.0007 (10)	0.0177 (8)	-0.0114 (10)
N1	0.0341 (14)	0.076 (2)	0.0502 (15)	-0.0136 (13)	0.0009 (12)	0.0058 (14)
N2	0.0438 (14)	0.0591 (16)	0.0439 (14)	-0.0010 (12)	0.0144 (11)	-0.0097 (12)
C1	0.053 (2)	0.077 (3)	0.071 (2)	-0.0121 (19)	-0.0019 (18)	0.006 (2)
C2	0.0490 (17)	0.0470 (17)	0.0483 (18)	-0.0062 (14)	0.0113 (14)	-0.0035 (14)
C3	0.0439 (16)	0.0499 (17)	0.0452 (16)	-0.0041 (13)	0.0176 (13)	0.0034 (14)
C4	0.071 (2)	0.063 (2)	0.069 (2)	0.0029 (18)	0.039 (2)	-0.0023 (18)
C5	0.064 (2)	0.076 (3)	0.110 (4)	0.019 (2)	0.052 (3)	0.016 (3)
C6	0.0366 (17)	0.080 (3)	0.089 (3)	0.0054 (17)	0.0247 (18)	0.019 (2)
C7	0.0334 (14)	0.0576 (18)	0.0536 (18)	-0.0082 (13)	0.0134 (13)	0.0112 (15)
C8	0.0327 (13)	0.0462 (15)	0.0385 (14)	-0.0042 (11)	0.0110 (11)	0.0070 (12)
C9	0.0397 (14)	0.0479 (15)	0.0325 (13)	-0.0044 (12)	0.0087 (11)	0.0030 (12)
C10	0.0490 (17)	0.064 (2)	0.0374 (15)	-0.0099 (16)	0.0078 (13)	-0.0025 (14)
C11	0.0408 (15)	0.0561 (18)	0.0430 (15)	0.0002 (14)	0.0087 (13)	-0.0020 (14)
C12	0.0429 (17)	0.0551 (19)	0.063 (2)	-0.0037 (14)	0.0151 (16)	-0.0039 (15)
C13	0.062 (2)	0.062 (2)	0.065 (2)	0.0093 (17)	0.0170 (18)	-0.0060 (17)
C14	0.089 (3)	0.056 (2)	0.078 (3)	0.006 (2)	0.033 (2)	0.003 (2)
C15	0.117 (5)	0.094 (4)	0.118 (4)	-0.012 (3)	0.044 (4)	0.018 (4)
C16	0.071 (2)	0.105 (3)	0.058 (2)	-0.005 (2)	0.039 (2)	-0.006 (2)
C17	0.0252 (12)	0.0562 (17)	0.0398 (15)	-0.0030 (13)	0.0104 (11)	-0.0064 (13)
C18	0.0264 (12)	0.0607 (18)	0.0370 (14)	-0.0035 (12)	0.0113 (11)	-0.0052 (13)
C19	0.0233 (12)	0.0588 (17)	0.0370 (13)	-0.0041 (12)	0.0091 (10)	-0.0037 (12)
C20	0.0232 (11)	0.0485 (15)	0.0384 (14)	-0.0016 (11)	0.0107 (10)	-0.0002 (12)

Geometric parameters (Å, °)

O1—C2	1.185 (4)	C6—C7	1.394 (6)
O2—C2	1.351 (4)	C7—C8	1.419 (4)
O2—C3	1.408 (4)	C8—C9	1.431 (5)
O3—C17	1.212 (3)	C9—C10	1.365 (4)
O4—H4A	0.894 (14)	C9—C11	1.508 (4)
O4—C17	1.256 (3)	C10—H10	0.9300

O5—C20	1.216 (3)	C11—H11A	0.9700
O6—C20	1.290 (3)	C11—H11B	0.9700
N1—H1	0.867 (14)	C11—C12	1.488 (5)
N1—C7	1.362 (5)	C12—H12A	0.9700
N1—C10	1.362 (5)	C12—H12B	0.9700
N2—H2	0.890 (14)	C13—H13A	0.9700
N2—C12	1.502 (4)	C13—H13B	0.9700
N2—C13	1.499 (5)	C13—C14	1.460 (6)
N2—C16	1.484 (4)	C14—H14	0.9300
C1—H1A	0.9600	C14—C15	1.292 (7)
C1—H1B	0.9600	C15—H15A	0.9300
C1—H1C	0.9600	C15—H15B	0.9300
C1—C2	1.499 (5)	C16—H16A	0.9600
C3—C4	1.372 (5)	C16—H16B	0.9600
C3—C8	1.396 (4)	C16—H16C	0.9600
C4—H4	0.9300	C17—C18	1.489 (3)
C4—C5	1.404 (6)	C18—H18	0.9300
C5—H5	0.9300	C18—C19	1.302 (4)
C5—C6	1.361 (7)	C19—H19	0.9300
C6—H6	0.9300	C19—C20	1.491 (3)
C2—O2—C3	117.2 (2)	C9—C10—H10	124.7
C17—O4—H4A	114 (3)	C9—C11—H11A	109.3
C7—N1—H1	126 (3)	C9—C11—H11B	109.3
C7—N1—C10	109.2 (3)	H11A—C11—H11B	107.9
C10—N1—H1	124 (3)	C12—C11—C9	111.7 (3)
C12—N2—H2	110 (3)	C12—C11—H11A	109.3
C13—N2—H2	105 (3)	C12—C11—H11B	109.3
C13—N2—C12	111.8 (3)	N2—C12—H12A	109.1
C16—N2—H2	106 (3)	N2—C12—H12B	109.1
C16—N2—C12	111.8 (3)	C11—C12—N2	112.7 (3)
C16—N2—C13	111.1 (3)	C11—C12—H12A	109.1
H1A—C1—H1B	109.5	C11—C12—H12B	109.1
H1A—C1—H1C	109.5	H12A—C12—H12B	107.8
H1B—C1—H1C	109.5	N2—C13—H13A	109.0
C2—C1—H1A	109.5	N2—C13—H13B	109.0
C2—C1—H1B	109.5	H13A—C13—H13B	107.8
C2—C1—H1C	109.5	C14—C13—N2	112.8 (3)
O1—C2—O2	123.5 (3)	C14—C13—H13A	109.0
O1—C2—C1	126.1 (3)	C14—C13—H13B	109.0
O2—C2—C1	110.4 (3)	C13—C14—H14	116.9
C4—C3—O2	118.5 (3)	C15—C14—C13	126.1 (5)
C4—C3—C8	121.4 (3)	C15—C14—H14	116.9
C8—C3—O2	119.9 (3)	C14—C15—H15A	120.0
C3—C4—H4	120.3	C14—C15—H15B	120.0
C3—C4—C5	119.4 (4)	H15A—C15—H15B	120.0
C5—C4—H4	120.3	N2—C16—H16A	109.5
C4—C5—H5	119.0	N2—C16—H16B	109.5

C6—C5—C4	121.9 (4)	N2—C16—H16C	109.5
C6—C5—H5	119.0	H16A—C16—H16B	109.5
C5—C6—H6	121.0	H16A—C16—H16C	109.5
C5—C6—C7	118.0 (3)	H16B—C16—H16C	109.5
C7—C6—H6	121.0	O3—C17—O4	124.6 (2)
N1—C7—C6	130.4 (3)	O3—C17—C18	120.1 (2)
N1—C7—C8	107.4 (3)	O4—C17—C18	115.3 (2)
C6—C7—C8	122.2 (3)	C17—C18—H18	118.0
C3—C8—C7	117.0 (3)	C19—C18—C17	124.0 (2)
C3—C8—C9	136.1 (3)	C19—C18—H18	118.0
C7—C8—C9	106.8 (3)	C18—C19—H19	118.6
C8—C9—C11	128.4 (3)	C18—C19—C20	122.8 (2)
C10—C9—C8	106.1 (3)	C20—C19—H19	118.6
C10—C9—C11	125.5 (3)	O5—C20—O6	125.1 (2)
N1—C10—C9	110.5 (3)	O5—C20—C19	121.3 (2)
N1—C10—H10	124.7	O6—C20—C19	113.6 (2)
O2—C3—C4—C5	-176.1 (3)	C6—C7—C8—C3	-1.0 (4)
O2—C3—C8—C7	176.5 (2)	C6—C7—C8—C9	179.9 (3)
O2—C3—C8—C9	-4.7 (5)	C7—N1—C10—C9	-0.9 (4)
O3—C17—C18—C19	-2.3 (6)	C7—C8—C9—C10	-0.1 (3)
O4—C17—C18—C19	176.4 (4)	C7—C8—C9—C11	177.7 (3)
N1—C7—C8—C3	178.7 (3)	C8—C3—C4—C5	-0.4 (5)
N1—C7—C8—C9	-0.4 (3)	C8—C9—C10—N1	0.6 (4)
N2—C13—C14—C15	125.8 (5)	C8—C9—C11—C12	142.7 (3)
C2—O2—C3—C4	-100.4 (3)	C9—C11—C12—N2	174.6 (3)
C2—O2—C3—C8	83.9 (4)	C10—N1—C7—C6	-179.6 (4)
C3—O2—C2—O1	-0.7 (5)	C10—N1—C7—C8	0.8 (4)
C3—O2—C2—C1	-180.0 (3)	C10—C9—C11—C12	-39.8 (4)
C3—C4—C5—C6	-0.1 (6)	C11—C9—C10—N1	-177.3 (3)
C3—C8—C9—C10	-179.0 (3)	C12—N2—C13—C14	-63.6 (4)
C3—C8—C9—C11	-1.1 (6)	C13—N2—C12—C11	158.9 (3)
C4—C3—C8—C7	0.9 (5)	C16—N2—C12—C11	-75.8 (4)
C4—C3—C8—C9	179.7 (3)	C16—N2—C13—C14	170.7 (3)
C4—C5—C6—C7	0.0 (6)	C17—C18—C19—C20	179.9 (3)
C5—C6—C7—N1	-179.0 (4)	C18—C19—C20—O5	-15.6 (5)
C5—C6—C7—C8	0.5 (5)	C18—C19—C20—O6	164.6 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O5 ⁱ	0.87 (1)	2.00 (2)	2.857 (3)	169 (4)
O4—H4A \cdots O6 ⁱⁱ	0.89 (1)	1.56 (2)	2.454 (3)	175 (6)

Symmetry codes: (i) $x-2, y, z-1$; (ii) $x-1, y, z$.

Bis{[2-(4-acetyloxy-1*H*-indol-3-yl)ethyl]diprop-2-enylazanium} but-2-enedioate-(*E*)-butenedioic acid (1/1) (III)*Crystal data* $2C_{18}H_{23}N_2O_2^+ \cdot C_4H_2O_4^{2-} \cdot C_4H_4O_4$ $M_r = 828.90$ Monoclinic, $C2/c$ $a = 23.6642$ (19) Å $b = 8.4204$ (7) Å $c = 23.4002$ (18) Å $\beta = 111.614$ (2)° $V = 4334.9$ (6) Å³ $Z = 4$ $F(000) = 1760$ $D_x = 1.270$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9906 reflections

 $\theta = 2.6$ – 24.9° $\mu = 0.09$ mm⁻¹ $T = 297$ K

Block, colorless

 $0.22 \times 0.2 \times 0.12$ mm*Data collection*Bruker D8 Venture CMOS
diffractometer φ and ω scansAbsorption correction: multi-scan
(SADABS; Bruker, 2018) $T_{\min} = 0.715$, $T_{\max} = 0.745$

99597 measured reflections

4126 independent reflections

3441 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.040$ $\theta_{\max} = 25.8^\circ$, $\theta_{\min} = 2.6^\circ$ $h = -28 \rightarrow 28$ $k = -10 \rightarrow 10$ $l = -28 \rightarrow 28$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.051$ $wR(F^2) = 0.140$ $S = 1.06$

4126 reflections

354 parameters

114 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0623P)^2 + 3.3312P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.50$ e Å⁻³ $\Delta\rho_{\min} = -0.29$ e Å⁻³

Extinction correction: SHELXL2018

(Sheldrick, 2015b),

 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0057 (13)

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O3	0.43377 (5)	0.84230 (16)	0.40787 (6)	0.0547 (4)	
O4	0.52519 (5)	0.82545 (19)	0.40300 (6)	0.0650 (4)	
N1	0.15205 (7)	0.5819 (2)	0.16972 (7)	0.0540 (4)	
H1	0.1284 (8)	0.542 (2)	0.1349 (6)	0.065*	
N2	0.40861 (6)	0.56750 (17)	0.34003 (6)	0.0444 (4)	
H2	0.4151 (9)	0.6559 (16)	0.3614 (8)	0.053*	
C3	0.19478 (8)	0.6147 (2)	0.33073 (8)	0.0533 (5)	
C4	0.14362 (9)	0.5733 (3)	0.34114 (10)	0.0683 (6)	

H4	0.144072	0.571251	0.381042	0.082*	
C5	0.09055 (9)	0.5341 (3)	0.29169 (12)	0.0705 (6)	
H5	0.055901	0.506800	0.299318	0.085*	
C6	0.08822 (8)	0.5348 (2)	0.23271 (10)	0.0590 (5)	
H6	0.052601	0.509456	0.200080	0.071*	
C7	0.14110 (7)	0.5749 (2)	0.22293 (8)	0.0467 (4)	
C8	0.19553 (7)	0.61618 (19)	0.27159 (8)	0.0432 (4)	
C9	0.24029 (7)	0.6461 (2)	0.24481 (8)	0.0450 (4)	
C10	0.21169 (8)	0.6216 (2)	0.18357 (9)	0.0537 (5)	
H10	0.230151	0.630485	0.154837	0.064*	
C11	0.30631 (7)	0.6867 (2)	0.27697 (9)	0.0496 (4)	
H11A	0.310383	0.771998	0.306092	0.060*	
H11B	0.323061	0.722895	0.247150	0.060*	
C12	0.34109 (7)	0.5424 (2)	0.31047 (9)	0.0480 (4)	
H12A	0.325670	0.511823	0.341969	0.058*	
H12B	0.333443	0.455047	0.281562	0.058*	
C16	0.43581 (9)	0.4308 (3)	0.38317 (11)	0.0664 (6)	
H16A	0.417335	0.427499	0.413909	0.080*	
H16B	0.425604	0.332482	0.360012	0.080*	
C17	0.50234 (11)	0.4390 (3)	0.41471 (13)	0.0871 (8)	
H17	0.519123	0.527455	0.438803	0.105*	
C18	0.53850 (14)	0.3276 (5)	0.41018 (19)	0.1316 (14)	
H18A	0.522600	0.238260	0.386311	0.158*	
H18B	0.580261	0.337274	0.430818	0.158*	
C19	0.48981 (7)	0.8722 (2)	0.42812 (8)	0.0467 (4)	
C20	0.51576 (7)	0.9709 (2)	0.48471 (8)	0.0479 (4)	
H20	0.557205	0.992472	0.499179	0.057*	
O5	0.6457 (5)	0.730 (3)	0.5379 (4)	0.097 (5)	0.48 (4)
O6	0.6402 (8)	0.822 (2)	0.4447 (8)	0.062 (2)	0.48 (4)
H6A	0.603390	0.828442	0.436178	0.094*	0.48 (4)
C21	0.6647 (8)	0.748 (3)	0.4963 (7)	0.060 (3)	0.48 (4)
O5A	0.6392 (3)	0.645 (2)	0.5186 (10)	0.103 (4)	0.52 (4)
O6A	0.6418 (7)	0.800 (3)	0.4512 (8)	0.084 (4)	0.52 (4)
H6AA	0.605462	0.793944	0.444863	0.126*	0.52 (4)
C21A	0.6724 (9)	0.727 (3)	0.5011 (8)	0.070 (4)	0.52 (4)
C22	0.73480 (9)	0.7230 (3)	0.51577 (9)	0.0637 (6)	
H22	0.755398	0.666681	0.551626	0.076*	0.48 (4)
H22A	0.757554	0.675587	0.553077	0.076*	0.52 (4)
C13	0.43825 (8)	0.5987 (3)	0.29456 (9)	0.0579 (5)	
H13A	0.470397	0.672837	0.316182	0.069*	0.099 (4)
H13B	0.458837	0.499336	0.294117	0.069*	0.099 (4)
H13C	0.427809	0.705354	0.278487	0.069*	0.901 (4)
H13D	0.481992	0.594839	0.315899	0.069*	0.901 (4)
C14	0.4188 (10)	0.652 (3)	0.2307 (5)	0.0769 (8)	0.099 (4)
H14	0.423405	0.761671	0.228839	0.092*	0.099 (4)
C15	0.397 (3)	0.592 (7)	0.1760 (14)	0.1028 (15)	0.099 (4)
H15A	0.390253	0.483222	0.170924	0.123*	0.099 (4)
H15B	0.388512	0.657311	0.141789	0.123*	0.099 (4)

C14A	0.42144 (12)	0.4880 (3)	0.24310 (12)	0.0769 (8)	0.901 (4)
H14A	0.428767	0.380233	0.251180	0.092*	0.901 (4)
C15A	0.3967 (3)	0.5342 (6)	0.18674 (15)	0.1028 (15)	0.901 (4)
H15C	0.389088	0.641456	0.177808	0.123*	0.901 (4)
H15D	0.386609	0.460156	0.155046	0.123*	0.901 (4)
O1	0.2254 (8)	0.8833 (10)	0.3924 (13)	0.099 (6)	0.38 (4)
O2	0.2527 (6)	0.645 (2)	0.3753 (9)	0.071 (5)	0.38 (4)
C1	0.3155 (7)	0.789 (2)	0.4602 (7)	0.066 (4)	0.38 (4)
H1A	0.333536	0.689257	0.477037	0.098*	0.38 (4)
H1B	0.313766	0.856311	0.492675	0.098*	0.38 (4)
H1C	0.339598	0.839519	0.440153	0.098*	0.38 (4)
C2	0.2529 (8)	0.7621 (19)	0.4148 (8)	0.064 (6)	0.38 (4)
O1A	0.2133 (4)	0.848 (2)	0.4172 (7)	0.102 (4)	0.62 (4)
O2A	0.2484 (4)	0.6422 (12)	0.3825 (6)	0.063 (2)	0.62 (4)
C1A	0.3206 (6)	0.772 (2)	0.4660 (6)	0.113 (5)	0.62 (4)
H1AA	0.350811	0.753864	0.448371	0.170*	0.62 (4)
H1AB	0.321755	0.687720	0.493898	0.170*	0.62 (4)
H1AC	0.328772	0.871404	0.487805	0.170*	0.62 (4)
C2A	0.2590 (5)	0.7784 (14)	0.4159 (6)	0.071 (4)	0.62 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0303 (6)	0.0649 (8)	0.0582 (7)	-0.0035 (5)	0.0039 (5)	-0.0155 (6)
O4	0.0370 (7)	0.0920 (11)	0.0605 (8)	-0.0001 (6)	0.0115 (6)	-0.0220 (7)
N1	0.0411 (8)	0.0576 (9)	0.0510 (9)	0.0042 (7)	0.0024 (6)	-0.0055 (7)
N2	0.0326 (7)	0.0479 (8)	0.0502 (8)	-0.0044 (6)	0.0122 (6)	-0.0050 (6)
C3	0.0375 (9)	0.0627 (11)	0.0553 (10)	0.0019 (8)	0.0119 (8)	-0.0016 (9)
C4	0.0538 (11)	0.0892 (16)	0.0675 (13)	-0.0008 (11)	0.0288 (10)	0.0034 (11)
C5	0.0405 (10)	0.0807 (15)	0.0945 (16)	-0.0076 (10)	0.0299 (11)	-0.0024 (12)
C6	0.0314 (8)	0.0566 (11)	0.0806 (14)	-0.0009 (8)	0.0108 (8)	-0.0072 (10)
C7	0.0343 (8)	0.0396 (9)	0.0584 (10)	0.0039 (6)	0.0079 (7)	-0.0025 (7)
C8	0.0313 (8)	0.0403 (8)	0.0528 (9)	0.0026 (6)	0.0095 (7)	-0.0019 (7)
C9	0.0348 (8)	0.0417 (9)	0.0553 (10)	0.0021 (7)	0.0128 (7)	-0.0009 (7)
C10	0.0468 (10)	0.0573 (11)	0.0553 (10)	0.0048 (8)	0.0170 (8)	0.0018 (8)
C11	0.0353 (8)	0.0457 (9)	0.0664 (11)	-0.0047 (7)	0.0170 (8)	-0.0052 (8)
C12	0.0307 (8)	0.0488 (9)	0.0624 (10)	-0.0065 (7)	0.0147 (7)	-0.0048 (8)
C16	0.0520 (11)	0.0612 (12)	0.0793 (14)	-0.0024 (9)	0.0163 (10)	0.0168 (10)
C17	0.0572 (13)	0.0821 (16)	0.0994 (18)	-0.0041 (12)	0.0022 (12)	0.0325 (14)
C18	0.0713 (18)	0.136 (3)	0.169 (4)	0.0369 (19)	0.021 (2)	0.068 (3)
C19	0.0323 (8)	0.0518 (10)	0.0467 (9)	0.0012 (7)	0.0035 (7)	-0.0023 (7)
C20	0.0288 (7)	0.0548 (10)	0.0505 (9)	-0.0047 (7)	0.0033 (6)	-0.0049 (8)
O5	0.053 (3)	0.178 (11)	0.073 (3)	0.018 (5)	0.037 (2)	0.035 (4)
O6	0.039 (4)	0.086 (4)	0.055 (4)	0.004 (3)	0.009 (3)	0.024 (3)
C21	0.021 (3)	0.104 (9)	0.054 (4)	0.014 (4)	0.014 (3)	0.030 (5)
O5A	0.055 (2)	0.139 (8)	0.120 (7)	-0.005 (3)	0.039 (3)	0.053 (6)
O6A	0.033 (4)	0.140 (11)	0.079 (6)	0.007 (4)	0.021 (4)	0.032 (5)
C21A	0.051 (8)	0.085 (5)	0.073 (6)	0.012 (5)	0.021 (5)	0.019 (5)

C22	0.0401 (10)	0.0906 (15)	0.0582 (11)	0.0058 (10)	0.0156 (8)	0.0138 (11)
C13	0.0387 (9)	0.0753 (13)	0.0602 (11)	-0.0093 (9)	0.0190 (8)	-0.0079 (10)
C14	0.0792 (17)	0.0819 (17)	0.0850 (19)	-0.0242 (14)	0.0481 (15)	-0.0265 (14)
C15	0.0831 (18)	0.165 (4)	0.0664 (19)	-0.026 (3)	0.0341 (17)	-0.027 (2)
C14A	0.0792 (17)	0.0819 (17)	0.0850 (19)	-0.0242 (14)	0.0481 (15)	-0.0265 (14)
C15A	0.0831 (18)	0.165 (4)	0.0664 (19)	-0.026 (3)	0.0341 (17)	-0.027 (2)
O1	0.087 (5)	0.069 (4)	0.116 (10)	-0.002 (3)	0.006 (6)	-0.008 (4)
O2	0.043 (4)	0.126 (10)	0.045 (4)	-0.007 (5)	0.015 (3)	-0.025 (5)
C1	0.052 (7)	0.099 (8)	0.046 (5)	-0.009 (6)	0.018 (6)	-0.016 (5)
C2	0.040 (6)	0.086 (11)	0.048 (7)	-0.005 (6)	-0.005 (5)	0.004 (6)
O1A	0.076 (3)	0.111 (6)	0.101 (5)	0.016 (3)	0.013 (3)	-0.032 (4)
O2A	0.040 (2)	0.090 (4)	0.052 (4)	0.012 (3)	0.009 (2)	-0.005 (3)
C1A	0.067 (5)	0.168 (12)	0.075 (5)	-0.018 (6)	-0.009 (4)	-0.013 (6)
C2A	0.066 (6)	0.079 (6)	0.070 (6)	-0.022 (4)	0.027 (5)	-0.014 (4)

Geometric parameters (Å, °)

O3—C19	1.2583 (19)	C20—H20	0.9300
O4—C19	1.251 (2)	O5—C21	1.223 (9)
N1—H1	0.868 (10)	O6—H6A	0.8200
N1—C7	1.363 (2)	O6—C21	1.289 (8)
N1—C10	1.368 (2)	C21—C22	1.564 (18)
N2—H2	0.878 (9)	O5A—C21A	1.221 (10)
N2—C12	1.5038 (19)	O6A—H6AA	0.8200
N2—C16	1.510 (2)	O6A—C21A	1.285 (8)
N2—C13	1.498 (2)	C21A—C22	1.388 (19)
C3—C4	1.365 (3)	C22—C22 ⁱⁱ	1.288 (4)
C3—C8	1.391 (3)	C22—H22	0.9300
C3—O2	1.407 (9)	C22—H22A	0.9300
C3—O2A	1.413 (6)	C13—H13A	0.9700
C4—H4	0.9300	C13—H13B	0.9700
C4—C5	1.398 (3)	C13—H13C	0.9700
C5—H5	0.9300	C13—H13D	0.9700
C5—C6	1.361 (3)	C13—C14	1.465 (10)
C6—H6	0.9300	C13—C14A	1.458 (3)
C6—C7	1.394 (3)	C14—H14	0.9300
C7—C8	1.413 (2)	C14—C15	1.294 (10)
C8—C9	1.438 (2)	C15—H15A	0.9300
C9—C10	1.357 (3)	C15—H15B	0.9300
C9—C11	1.503 (2)	C14A—H14A	0.9300
C10—H10	0.9300	C14A—C15A	1.290 (4)
C11—H11A	0.9700	C15A—H15C	0.9300
C11—H11B	0.9700	C15A—H15D	0.9300
C11—C12	1.514 (2)	O1—C2	1.220 (10)
C12—H12A	0.9700	O2—C2	1.348 (9)
C12—H12B	0.9700	C1—H1A	0.9600
C16—H16A	0.9700	C1—H1B	0.9600
C16—H16B	0.9700	C1—H1C	0.9600

C16—C17	1.474 (3)	C1—C2	1.489 (9)
C17—H17	0.9300	O1A—C2A	1.239 (9)
C17—C18	1.300 (4)	O2A—C2A	1.359 (7)
C18—H18A	0.9300	C1A—H1AA	0.9600
C18—H18B	0.9300	C1A—H1AB	0.9600
C19—C20	1.491 (2)	C1A—H1AC	0.9600
C20—C20 ⁱ	1.304 (3)	C1A—C2A	1.498 (8)
C7—N1—H1	124.6 (14)	C19—C20—H20	117.8
C7—N1—C10	108.71 (15)	C20 ⁱ —C20—C19	124.40 (19)
C10—N1—H1	124.6 (14)	C20 ⁱ —C20—H20	117.8
C12—N2—H2	108.3 (13)	C21—O6—H6A	109.5
C12—N2—C16	108.62 (13)	O5—C21—O6	129.4 (19)
C16—N2—H2	108.9 (13)	O5—C21—C22	114.3 (14)
C13—N2—H2	103.1 (13)	O6—C21—C22	113.7 (10)
C13—N2—C12	113.22 (14)	C21A—O6A—H6AA	109.5
C13—N2—C16	114.38 (15)	O5A—C21A—O6A	111 (2)
C4—C3—C8	121.14 (17)	O5A—C21A—C22	131.5 (18)
C4—C3—O2	126.9 (12)	O6A—C21A—C22	115.3 (11)
C4—C3—O2A	117.6 (8)	C21—C22—H22	118.6
C8—C3—O2	111.7 (12)	C21A—C22—H22A	115.9
C8—C3—O2A	121.0 (8)	C22 ⁱⁱ —C22—C21	122.7 (5)
C3—C4—H4	120.1	C22 ⁱⁱ —C22—C21A	128.2 (7)
C3—C4—C5	119.9 (2)	C22 ⁱⁱ —C22—H22	118.6
C5—C4—H4	120.1	C22 ⁱⁱ —C22—H22A	115.9
C4—C5—H5	119.1	N2—C13—H13A	103.0
C6—C5—C4	121.79 (18)	N2—C13—H13B	103.0
C6—C5—H5	119.1	N2—C13—H13C	108.6
C5—C6—H6	121.2	N2—C13—H13D	108.6
C5—C6—C7	117.65 (18)	H13A—C13—H13B	105.1
C7—C6—H6	121.2	H13C—C13—H13D	107.6
N1—C7—C6	130.13 (17)	C14—C13—N2	136.6 (9)
N1—C7—C8	107.57 (15)	C14—C13—H13A	103.0
C6—C7—C8	122.29 (18)	C14—C13—H13B	103.0
C3—C8—C7	117.24 (15)	C14A—C13—N2	114.71 (17)
C3—C8—C9	135.79 (15)	C14A—C13—H13C	108.6
C7—C8—C9	106.93 (15)	C14A—C13—H13D	108.6
C8—C9—C11	128.22 (16)	C13—C14—H14	110.7
C10—C9—C8	105.82 (15)	C15—C14—C13	139 (3)
C10—C9—C11	125.87 (16)	C15—C14—H14	110.7
N1—C10—H10	124.5	C14—C15—H15A	120.0
C9—C10—N1	110.92 (16)	C14—C15—H15B	120.0
C9—C10—H10	124.5	H15A—C15—H15B	120.0
C9—C11—H11A	109.6	C13—C14A—H14A	118.8
C9—C11—H11B	109.6	C15A—C14A—C13	122.3 (3)
C9—C11—C12	110.08 (14)	C15A—C14A—H14A	118.8
H11A—C11—H11B	108.2	C14A—C15A—H15C	120.0
C12—C11—H11A	109.6	C14A—C15A—H15D	120.0

C12—C11—H11B	109.6	H15C—C15A—H15D	120.0
N2—C12—C11	114.08 (14)	C2—O2—C3	113.5 (14)
N2—C12—H12A	108.7	H1A—C1—H1B	109.5
N2—C12—H12B	108.7	H1A—C1—H1C	109.5
C11—C12—H12A	108.7	H1B—C1—H1C	109.5
C11—C12—H12B	108.7	C2—C1—H1A	109.5
H12A—C12—H12B	107.6	C2—C1—H1B	109.5
N2—C16—H16A	108.7	C2—C1—H1C	109.5
N2—C16—H16B	108.7	O1—C2—O2	117 (2)
H16A—C16—H16B	107.6	O1—C2—C1	114.3 (18)
C17—C16—N2	114.37 (17)	O2—C2—C1	110.6 (12)
C17—C16—H16A	108.7	C2A—O2A—C3	123.3 (8)
C17—C16—H16B	108.7	H1AA—C1A—H1AB	109.5
C16—C17—H17	118.7	H1AA—C1A—H1AC	109.5
C18—C17—C16	122.6 (3)	H1AB—C1A—H1AC	109.5
C18—C17—H17	118.7	C2A—C1A—H1AA	109.5
C17—C18—H18A	120.0	C2A—C1A—H1AB	109.5
C17—C18—H18B	120.0	C2A—C1A—H1AC	109.5
H18A—C18—H18B	120.0	O1A—C2A—O2A	115.7 (14)
O3—C19—C20	118.57 (15)	O1A—C2A—C1A	127.1 (11)
O4—C19—O3	123.72 (16)	O2A—C2A—C1A	110.0 (9)
O4—C19—C20	117.70 (14)		
O3—C19—C20—C20 ⁱ	0.2 (3)	C8—C3—O2—C2	128.5 (19)
O4—C19—C20—C20 ⁱ	179.3 (2)	C8—C3—O2A—C2A	107.5 (16)
N1—C7—C8—C3	-179.21 (16)	C8—C9—C10—N1	1.3 (2)
N1—C7—C8—C9	-0.90 (18)	C8—C9—C11—C12	71.7 (2)
N2—C16—C17—C18	-121.8 (3)	C9—C11—C12—N2	175.40 (14)
N2—C13—C14—C15	-86 (5)	C10—N1—C7—C6	-177.82 (19)
N2—C13—C14A—C15A	121.5 (3)	C10—N1—C7—C8	1.7 (2)
C3—C4—C5—C6	0.4 (4)	C10—C9—C11—C12	-104.3 (2)
C3—C8—C9—C10	177.6 (2)	C11—C9—C10—N1	178.07 (16)
C3—C8—C9—C11	1.0 (3)	C12—N2—C16—C17	179.1 (2)
C3—O2—C2—O1	-47 (4)	C12—N2—C13—C14	20.0 (14)
C3—O2—C2—C1	-179.5 (18)	C12—N2—C13—C14A	-48.3 (2)
C3—O2A—C2A—O1A	29 (3)	C16—N2—C12—C11	167.33 (16)
C3—O2A—C2A—C1A	-177.9 (14)	C16—N2—C13—C14	145.2 (14)
C4—C3—C8—C7	0.7 (3)	C16—N2—C13—C14A	76.8 (2)
C4—C3—C8—C9	-177.0 (2)	O5—C21—C22—C22 ⁱⁱ	-160.9 (18)
C4—C3—O2—C2	-57 (3)	O6—C21—C22—C22 ⁱⁱ	3 (2)
C4—C3—O2A—C2A	-78.0 (17)	O5A—C21A—C22—C22 ⁱⁱ	158 (2)
C4—C5—C6—C7	0.6 (3)	O6A—C21A—C22—C22 ⁱⁱ	-4 (3)
C5—C6—C7—N1	178.49 (19)	C13—N2—C12—C11	-64.5 (2)
C5—C6—C7—C8	-1.0 (3)	C13—N2—C16—C17	51.5 (3)
C6—C7—C8—C3	0.4 (3)	O2—C3—C4—C5	-174.8 (10)
C6—C7—C8—C9	178.68 (16)	O2—C3—C8—C7	175.3 (9)
C7—N1—C10—C9	-2.0 (2)	O2—C3—C8—C9	-2.4 (9)
C7—C8—C9—C10	-0.25 (19)	O2A—C3—C4—C5	-175.5 (5)

C7—C8—C9—C11	-176.89 (16)	O2A—C3—C8—C7	175.0 (5)
C8—C3—C4—C5	-1.1 (3)	O2A—C3—C8—C9	-2.7 (6)

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1...O3 ⁱⁱⁱ	0.87 (1)	2.22 (2)	2.962 (2)	144 (2)
N2—H2...O3	0.88 (1)	1.87 (1)	2.7446 (19)	177 (2)
O6—H6A...O4	0.82	1.72	2.530 (17)	168
O6A—H6AA...O4	0.82	1.81	2.577 (16)	156

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