

**(R)-Phenylethylammonium (R)-4-chloro-  
mandelate**Quan He,<sup>a</sup> Michael C. Jennings,<sup>b\*</sup> Sohrab Rohani,<sup>a</sup> Jesse Zhu<sup>a</sup> and Hassan Gomaa<sup>a</sup><sup>a</sup>Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, Ontario, Canada N6A 5B9, and <sup>b</sup>Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

Correspondence e-mail: mjenning@uwo.ca

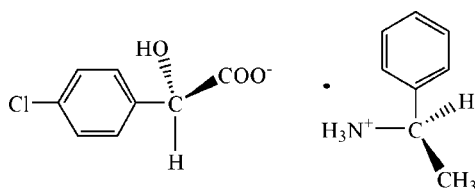
Received 14 September 2007; accepted 24 September 2007

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.038;  $wR$  factor = 0.095; data-to-parameter ratio = 14.2.

Optical resolution of a racemic mixture of ( $\pm$ )-4-chloro-mandelic acid (4-CIMA) was obtained using (*R*)-phenylethylamine (*R*-PEA) as a resolving agent. A pair of diastereomeric salts (*R*-4-CIMA·*R*-PEA and *S*-4-CIMA·*R*-PEA) had significantly different solubilities and allowed optically pure crystals of the title complex, (*R*)-phenylethylammonium (*R*)-2-(4-chlorophenyl)-2-hydroxyacetate,  $\text{C}_8\text{H}_{12}\text{N}^+\cdot\text{C}_8\text{H}_6\text{ClO}_3^-$  or  $[(R)\text{-C}_6\text{H}_5\text{C}(\text{H})\text{CH}_3\text{NH}_3][(\text{R})\text{-4-ClC}_6\text{H}_4\text{C}(\text{H})(\text{OH})\text{CO}_2]$ , to be isolated. The crystal structure of the enantiomeric *S,S* analogue has been published previously [Kinbara, Tagawa & Saigo (2001). *Tetrahedron Asymmetry*, **12**, 2927–2930]. In the title crystal structure, a two-dimensional network, perpendicular to the *c* axis, is formed *via* intermolecular hydrogen bonds.

**Related literature**

For background information, see: Adams *et al.* (2002); Huang *et al.* (2005); Yamaguchi *et al.* (2002); Langkilde *et al.* (2002); Hu *et al.* (2004). The crystal structure of the *S,S* enantiomer is isomorphous and is described briefly as a preliminary result by Kinbara *et al.* (2001).

**Experimental***Crystal data*
 $\text{C}_8\text{H}_{12}\text{N}^+\cdot\text{C}_8\text{H}_6\text{ClO}_3^-$   
 $M_r = 307.76$ 

 Orthorhombic,  $P2_12_12_1$   
 $a = 6.8848$  (3) Å

 $b = 8.3979$  (3) Å  
 $c = 26.9433$  (10) Å  
 $V = 1557.80$  (11) Å<sup>3</sup>  
 $Z = 4$ 

 Mo  $K\alpha$  radiation  
 $\mu = 0.25$  mm<sup>-1</sup>  
 $T = 296$  (2) K  
 $0.40 \times 0.13 \times 0.05$  mm
*Data collection*
 Nonius KappaCCD diffractometer  
 Absorption correction: multi-scan  
 (SORTAV; Blessing, 1995)  
 $T_{\min} = 0.838$ ,  $T_{\max} = 0.988$   
 18157 measured reflections  
 2731 independent reflections  
 2086 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.055$ 
*Refinement*
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.095$   
 $S = 1.03$   
 2731 reflections  
 193 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.15$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.19$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 1121 Friedel pairs  
 Flack parameter:  $-0.07$  (10)
**Table 1**

Hydrogen-bond geometry (Å, °).

<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>
O9—H9A···O11 <sup>i</sup>	0.82	2.09	2.848 (2)	154
N13—H13A···O12	0.89	2.00	2.836 (2)	157
N13—H13B···O11 <sup>ii</sup>	0.89	1.99	2.869 (3)	167
N13—H13C···O12 <sup>iii</sup>	0.89	2.04	2.878 (3)	156

Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{5}{2}, -z$ ; (ii)  $x - \frac{1}{2}, -y + \frac{3}{2}, -z$ ; (iii)  $x + \frac{1}{2}, -y + \frac{3}{2}, -z$ .

Data collection: COLLECT (Nonius, 2001); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL/PC (Sheldrick, 2001); software used to prepare material for publication: SHELXTL/PC.

This work was partially supported by Ningbo Natural Science Fund (2005B100085 and 2005 A620017)

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2509).

**References**

- Adams, A. D., Jones, A. B. & Berger, J. P. (2002). Patent No. WO 02064094.  
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Huang, H. R., Xu, J. H. & Xu, Y. (2005). *Tetrahedron Asymmetry*, **16**, 2113–2117.  
 Hu, Z.-Q., Xu, D.-J. & Xu, Y.-Z. (2004). *Acta Cryst.* **E60**, o269–o271.  
 Kinbara, K., Tagawa, Y. & Saigo, K. (2001). *Tetrahedron Asymmetry*, **12**, 2927–2930.  
 Langkilde, A., Oddershede, J. & Larsen, S. (2002). *Acta Cryst.* **B58**, 1044–1050.  
 Nonius (2001). COLLECT. Nonius BV, Delft, The Netherlands.  
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.  
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.  
 Sheldrick, G. M. (2001). SHELXTL/PC. Version 6.1 for Windows NT. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Yamaguchi, Y., Hamanaka, K. & Shibuya, N. (2002). Japanese Patent No. JP 2002030032.

**supplementary materials**

*Acta Cryst.* (2007). E63, o4199 [ doi:10.1107/S160053680704696X ]

## (*R*)-Phenylethylammonium (*R*)-4-chloromandelate

Q. He, M. C. Jennings, S. Rohani, J. Zhu and H. Gomaa

### Comment

Optically active (*R*)-4-Chloromandelic acid (R4-CIMA), being a significant chiral intermediate, has been widely used to synthesize many new pharmaceuticals (Adams *et al.*, 2002). Huang *et al.* (2005) prepared (*R*)-4-CIMA by enantioselective degradation of racemates with newly isolated *Pseudomonas putida*. Yamaguchi *et al.* (2002) carried out the optical resolution of racemic organic acids using optically active 4-amino-2-methyl-butan-1-ol as a resolving agent in 2-propanol solvent. However, there are significant drawbacks among the above mentioned methods such as low yield and the high cost of resolving agents. Our lab is searching for economically feasible methods.

In the investigation of the optical resolution of racemic 4-Chloromandelic acid by (*R*)-Phenylethylamine, crystals of (*R*)-Phenylethylamine-(*R*)-4-Chloromandelic acid (R4-CIMA·*R*-PEA), were obtained from a methanol solution containing racemic 4-Chloromandelic acid and (*R*)-Phenylethylamine. Herein we present the structure of R4-CIMA·*R*-PEA showing the successful optical resolution. The crystal structure of the enantiomeric (*S,S*) analogue has previously been published (Kinbara *et al.*, 2001).

The title complex consists of an ion pair; an amine cation and a carboxylate anion. The stereochemistry of each of the ions is successfully resolved (see: Flack parameter (Flack, 1983)) to be the *R* enantiomer. Three N—H atoms and a single O—H atom show close contacts to adjacent carboxylate O atoms. Thus, a two-dimensional network of H-bonding is observed. This presumably gives rise to the lower solubility of this product as compared to the *S,S*-CIMA,*R*-PEA product. At present, we are attempting to grow single crystals of the *S,R* product.

### Experimental

To a solution of racemic (+/-)-4-CIMA (8.4 g, 0.045 mol) in 72 ml methanol, was gradually added (5.7 mL, 0.045 mol) *R*-PEA. A white crystalline solid appeared. The mixture was heated to 333 K using a water bath and the solid dissolved. The solution was then allowed to stand at 333 K for 30 minutes and subsequently cooled slowly to 295 K. After standing at 295 K for 60 minutes, the precipitate was collected and washed twice with methanol. The filtered precipitate was recrystallized in methanol to give the optically pure salt *R*-4-CIMA·*R*-PEA (3.1 g, 45% yield). X-ray quality crystals of *R*-4-CIMA·*R*-PEA were grown from iso-propanol solution by slow evaporation at room temperature.

### Refinement

All H atoms were positioned geometrically and constrained as riding atoms with C—H = 0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for methyne H atoms and C—H = 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic H atoms and O—H = 0.82 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for hydroxyl H atoms and N—H = 0.89 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for amine H atoms.

## Figures

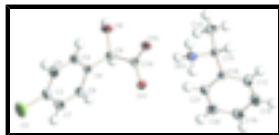


Fig. 1. The molecular structure of the title compound with 30% probability displacement ellipsoids and the atom labelling scheme.

## (*R*)-phenylethylaminium (*R*)-2-(4-chlorophenyl)-2-hydroxyacetate,

### Crystal data

$C_8H_{12}N^+ \cdot C_8H_6ClO_3^-$	$F_{000} = 648$
$M_r = 307.76$	$D_x = 1.312 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
Hall symbol: P 2ac 2ab	$\lambda = 0.71073 \text{ \AA}$
$a = 6.8848 (3) \text{ \AA}$	Cell parameters from 23622 reflections
$b = 8.3979 (3) \text{ \AA}$	$\theta = 2.0\text{--}27.5^\circ$
$c = 26.9433 (10) \text{ \AA}$	$\mu = 0.25 \text{ mm}^{-1}$
$V = 1557.80 (11) \text{ \AA}^3$	$T = 296 (2) \text{ K}$
$Z = 4$	Rod, colourless
	$0.40 \times 0.13 \times 0.05 \text{ mm}$

### Data collection

Nonius KappaCCD diffractometer	2731 independent reflections
Radiation source: fine-focus sealed tube	2086 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.055$
$T = 296(2) \text{ K}$	$\theta_{\text{max}} = 25.0^\circ$
$\varphi$ scans, and $\omega$ scans with $\kappa$ offsets	$\theta_{\text{min}} = 2.9^\circ$
Absorption correction: multi-scan from symmetry-related measurements (SORTAV; Blessing, 1995)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.838$ , $T_{\text{max}} = 0.988$	$k = -9 \rightarrow 9$
18157 measured reflections	$l = -32 \rightarrow 20$

### Refinement

Refinement on $F^2$	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.2438P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.095$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.15 \text{ e \AA}^{-3}$
2731 reflections	$\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$
	Extinction correction: SHELXL97 (Sheldrick, 1997),
	$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

193 parameters  
 Primary atom site location: structure-invariant direct methods  
 Secondary atom site location: difference Fourier map  
 Hydrogen site location: inferred from neighbouring sites  
 Extinction coefficient: 0.0116 (19)  
 Absolute structure: Flack (1983), 1121 Friedel pairs  
 Flack parameter: -0.07 (10)

*Special details*

**Experimental.** M.P. 469 K. The specific rotation was  $[\alpha]_D^{20} = -48.5^\circ$  ( $c=1$ ,  $C_2H_5OH$ ), determined using a WZZ-1S Digital Polarimeter;  $^1H$ -NMR ( $d_6$ -DMSO/TMS):  $\delta$  1.41 (d, 3H,  $CH_3$ ), 4.29 (m, 1H,  $CHNH_2$ ), 4.53 (s, 1H,  $CHOH$ ), 7.27–7.44 (m, 9H,  $C_6H_5$  and  $C_6H_4Cl$ ) measured using an AVANCE 500 MHz NMR (BRUKER). IR (KBr): 3301(*m*), 3036(*s*), 2535(*m*), 1610(*s*), 1576(*s*), 1531(*s*), 1383(*s*), 1193(*m*), 1072(*s*), 776(*s*), 705(*s*), 553(*m*), 478(*m*), 446(*m*) measured using a NICOLET 55XC. Elemental analysis: Calc'd for  $C_{16}H_{18}NO_3Cl$  (FW 307.8) C: 62.40, H: 5.85, N: 4.55; Found C: 62.71, H: 6.26, N: 4.48 using a Elementar Vario EL.

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

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{iso}^*/U_{eq}$
Cl1	1.08733 (15)	1.26848 (13)	-0.22906 (3)	0.1093 (4)
C2	0.9516 (4)	1.2426 (3)	-0.17511 (10)	0.0619 (7)
C3	0.7898 (4)	1.1480 (3)	-0.17627 (10)	0.0661 (8)
H3A	0.7535	1.0971	-0.2055	0.079*
C4	0.6809 (4)	1.1287 (3)	-0.13362 (9)	0.0537 (6)
H4A	0.5702	1.0653	-0.1344	0.064*
C5	0.7339 (3)	1.2022 (2)	-0.08997 (8)	0.0403 (5)
C6	0.8988 (4)	1.2948 (3)	-0.08991 (10)	0.0530 (6)
H6A	0.9373	1.3442	-0.0606	0.064*
C7	1.0087 (4)	1.3160 (3)	-0.13242 (11)	0.0666 (8)
H7A	1.1195	1.3792	-0.1319	0.080*
C8	0.6149 (3)	1.1803 (3)	-0.04321 (8)	0.0427 (6)
H8A	0.6380	1.2723	-0.0216	0.051*
O9	0.4138 (2)	1.1733 (2)	-0.05381 (6)	0.0592 (5)
H9A	0.3595	1.2511	-0.0417	0.089*
C10	0.6798 (3)	1.0312 (3)	-0.01565 (8)	0.0392 (5)
O11	0.8499 (2)	1.03549 (18)	0.00208 (6)	0.0487 (4)
O12	0.5668 (2)	0.91601 (18)	-0.01150 (6)	0.0516 (4)
N13	0.6696 (3)	0.6352 (2)	0.04075 (7)	0.0461 (5)
H13A	0.6670	0.7336	0.0285	0.069*
H13B	0.5842	0.5749	0.0246	0.069*

## supplementary materials

---

H13C	0.7881	0.5946	0.0371	0.069*
C14	0.4278 (4)	0.7292 (3)	0.10083 (10)	0.0608 (7)
H14A	0.4446	0.8374	0.0902	0.091*
H14B	0.3895	0.7275	0.1351	0.091*
H14C	0.3292	0.6793	0.0810	0.091*
C15	0.6183 (3)	0.6394 (3)	0.09474 (8)	0.0455 (6)
H15A	0.5985	0.5297	0.1060	0.055*
C16	0.7750 (3)	0.7132 (3)	0.12610 (9)	0.0445 (6)
C17	0.8086 (4)	0.6529 (3)	0.17348 (9)	0.0606 (7)
H17A	0.7429	0.5622	0.1840	0.073*
C18	0.9392 (5)	0.7270 (4)	0.20491 (10)	0.0721 (8)
H18A	0.9602	0.6861	0.2365	0.087*
C19	1.0372 (4)	0.8594 (4)	0.18997 (11)	0.0664 (8)
H19A	1.1238	0.9094	0.2114	0.080*
C20	1.0075 (4)	0.9186 (3)	0.14321 (11)	0.0634 (8)
H20A	1.0755	1.0082	0.1328	0.076*
C21	0.8777 (4)	0.8465 (3)	0.11138 (9)	0.0530 (7)
H21A	0.8591	0.8880	0.0797	0.064*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.1089 (8)	0.1380 (9)	0.0811 (6)	0.0112 (7)	0.0429 (5)	0.0314 (6)
C2	0.0596 (18)	0.0677 (18)	0.0583 (17)	0.0094 (16)	0.0110 (14)	0.0151 (15)
C3	0.076 (2)	0.0736 (18)	0.0484 (16)	-0.0007 (17)	0.0007 (15)	-0.0050 (15)
C4	0.0510 (15)	0.0571 (15)	0.0531 (15)	-0.0083 (13)	-0.0019 (14)	-0.0021 (13)
C5	0.0368 (12)	0.0369 (12)	0.0471 (13)	0.0010 (10)	-0.0021 (11)	0.0029 (11)
C6	0.0498 (15)	0.0539 (14)	0.0552 (15)	-0.0087 (13)	-0.0040 (13)	0.0047 (12)
C7	0.0532 (16)	0.0677 (19)	0.079 (2)	-0.0111 (14)	0.0051 (16)	0.0172 (16)
C8	0.0373 (13)	0.0398 (13)	0.0509 (14)	0.0030 (10)	-0.0009 (11)	-0.0044 (10)
O9	0.0358 (9)	0.0656 (11)	0.0760 (12)	0.0102 (9)	0.0029 (9)	-0.0010 (9)
C10	0.0379 (14)	0.0408 (13)	0.0390 (12)	0.0012 (11)	0.0021 (11)	-0.0069 (10)
O11	0.0426 (10)	0.0503 (9)	0.0532 (10)	0.0008 (8)	-0.0060 (8)	0.0020 (7)
O12	0.0429 (9)	0.0430 (8)	0.0690 (11)	-0.0065 (8)	-0.0004 (9)	0.0057 (8)
N13	0.0381 (11)	0.0452 (11)	0.0551 (12)	0.0027 (9)	-0.0016 (9)	-0.0044 (9)
C14	0.0422 (14)	0.0654 (17)	0.0749 (18)	0.0017 (14)	0.0066 (13)	-0.0155 (14)
C15	0.0463 (14)	0.0388 (12)	0.0514 (14)	-0.0045 (11)	0.0062 (12)	-0.0013 (11)
C16	0.0396 (13)	0.0439 (12)	0.0501 (14)	0.0039 (11)	0.0051 (11)	-0.0029 (12)
C17	0.0684 (18)	0.0593 (15)	0.0541 (16)	-0.0036 (15)	0.0061 (14)	0.0066 (14)
C18	0.086 (2)	0.080 (2)	0.0507 (16)	0.008 (2)	-0.0072 (16)	-0.0019 (15)
C19	0.0624 (18)	0.0704 (18)	0.0664 (18)	0.0044 (16)	-0.0123 (15)	-0.0148 (16)
C20	0.0522 (17)	0.0576 (16)	0.080 (2)	-0.0091 (14)	-0.0056 (16)	-0.0010 (15)
C21	0.0511 (16)	0.0511 (14)	0.0568 (15)	-0.0078 (14)	-0.0065 (13)	0.0081 (12)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

C11—C2	1.742 (3)	N13—H13B	0.8900
C2—C7	1.363 (4)	N13—H13C	0.8900
C2—C3	1.369 (4)	C14—C15	1.521 (3)

C3—C4	1.381 (4)	C14—H14A	0.9600
C3—H3A	0.9300	C14—H14B	0.9600
C4—C5	1.377 (3)	C14—H14C	0.9600
C4—H4A	0.9300	C15—C16	1.504 (3)
C5—C6	1.376 (3)	C15—H15A	0.9800
C5—C8	1.514 (3)	C16—C21	1.383 (3)
C6—C7	1.384 (4)	C16—C17	1.393 (3)
C6—H6A	0.9300	C17—C18	1.383 (4)
C7—H7A	0.9300	C17—H17A	0.9300
C8—O9	1.415 (3)	C18—C19	1.361 (4)
C8—C10	1.523 (3)	C18—H18A	0.9300
C8—H8A	0.9800	C19—C20	1.370 (4)
O9—H9A	0.8200	C19—H19A	0.9300
C10—O12	1.247 (3)	C20—C21	1.378 (3)
C10—O11	1.265 (3)	C20—H20A	0.9300
N13—C15	1.497 (3)	C21—H21A	0.9300
N13—H13A	0.8900		
C7—C2—C3	121.1 (3)	H13A—N13—H13C	109.5
C7—C2—C11	119.6 (2)	H13B—N13—H13C	109.5
C3—C2—C11	119.3 (2)	C15—C14—H14A	109.5
C2—C3—C4	119.4 (3)	C15—C14—H14B	109.5
C2—C3—H3A	120.3	H14A—C14—H14B	109.5
C4—C3—H3A	120.3	C15—C14—H14C	109.5
C5—C4—C3	120.9 (2)	H14A—C14—H14C	109.5
C5—C4—H4A	119.5	H14B—C14—H14C	109.5
C3—C4—H4A	119.5	N13—C15—C16	112.72 (19)
C6—C5—C4	118.2 (2)	N13—C15—C14	108.7 (2)
C6—C5—C8	120.9 (2)	C16—C15—C14	110.69 (18)
C4—C5—C8	120.9 (2)	N13—C15—H15A	108.2
C5—C6—C7	121.5 (2)	C16—C15—H15A	108.2
C5—C6—H6A	119.2	C14—C15—H15A	108.2
C7—C6—H6A	119.2	C21—C16—C17	118.2 (2)
C2—C7—C6	118.9 (3)	C21—C16—C15	122.6 (2)
C2—C7—H7A	120.6	C17—C16—C15	119.0 (2)
C6—C7—H7A	120.6	C18—C17—C16	120.3 (3)
O9—C8—C5	111.52 (18)	C18—C17—H17A	119.8
O9—C8—C10	110.60 (18)	C16—C17—H17A	119.8
C5—C8—C10	110.28 (18)	C19—C18—C17	120.6 (3)
O9—C8—H8A	108.1	C19—C18—H18A	119.7
C5—C8—H8A	108.1	C17—C18—H18A	119.7
C10—C8—H8A	108.1	C18—C19—C20	119.6 (3)
C8—O9—H9A	109.5	C18—C19—H19A	120.2
O12—C10—O11	124.5 (2)	C20—C19—H19A	120.2
O12—C10—C8	119.9 (2)	C19—C20—C21	120.7 (3)
O11—C10—C8	115.61 (19)	C19—C20—H20A	119.7
C15—N13—H13A	109.5	C21—C20—H20A	119.7
C15—N13—H13B	109.5	C20—C21—C16	120.6 (2)
H13A—N13—H13C	109.5	C20—C21—H21A	119.7
C15—N13—H13C	109.5	C16—C21—H21A	119.7

## supplementary materials

---

C7—C2—C3—C4	1.1 (4)	C5—C8—C10—O12	-114.3 (2)
C11—C2—C3—C4	-179.3 (2)	O9—C8—C10—O11	-169.88 (19)
C2—C3—C4—C5	-0.6 (4)	C5—C8—C10—O11	66.3 (2)
C3—C4—C5—C6	-0.3 (4)	N13—C15—C16—C21	40.7 (3)
C3—C4—C5—C8	-179.7 (2)	C14—C15—C16—C21	-81.2 (3)
C4—C5—C6—C7	0.7 (3)	N13—C15—C16—C17	-144.3 (2)
C8—C5—C6—C7	-179.9 (2)	C14—C15—C16—C17	93.7 (3)
C3—C2—C7—C6	-0.7 (4)	C21—C16—C17—C18	1.1 (4)
C11—C2—C7—C6	179.7 (2)	C15—C16—C17—C18	-174.1 (2)
C5—C6—C7—C2	-0.2 (4)	C16—C17—C18—C19	-0.3 (4)
C6—C5—C8—O9	143.6 (2)	C17—C18—C19—C20	-0.7 (4)
C4—C5—C8—O9	-37.0 (3)	C18—C19—C20—C21	0.8 (4)
C6—C5—C8—C10	-93.1 (2)	C19—C20—C21—C16	0.1 (4)
C4—C5—C8—C10	86.3 (3)	C17—C16—C21—C20	-1.0 (4)
O9—C8—C10—O12	9.6 (3)	C15—C16—C21—C20	174.0 (2)

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9—H9A $\cdots$ O11 <sup>i</sup>	0.82	2.09	2.848 (2)	154
N13—H13A $\cdots$ O12	0.89	2.00	2.836 (2)	157
N13—H13B $\cdots$ O11 <sup>ii</sup>	0.89	1.99	2.869 (3)	167
N13—H13C $\cdots$ O12 <sup>iii</sup>	0.89	2.04	2.878 (3)	156

Symmetry codes: (i)  $x-1/2, -y+5/2, -z$ ; (ii)  $x-1/2, -y+3/2, -z$ ; (iii)  $x+1/2, -y+3/2, -z$ .



Fig. 1

