

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

3-Chloroanilinium 4-methylbenzenesulfonate

 Jerry P. Jasinski,^{a*} James A. Golen,^a A. S. Praveen,^b
 H. S. Yathirajan^b and B. Narayana^c

^aDepartment of Chemistry, Keene State College, 229 Main Street, Keene, NH 03435-2001, USA, ^bDepartment of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, India, and ^cDepartment of Studies in Chemistry, Mangalore University, Mangalagangotri, 574 199, India
 Correspondence e-mail: jjasinski@keene.edu

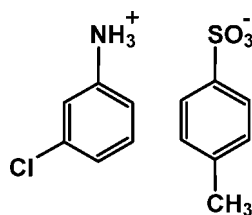
Received 5 September 2011; accepted 5 October 2011

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.037; wR factor = 0.109; data-to-parameter ratio = 17.7.

In the crystal structure of the title salt, $\text{C}_6\text{H}_7\text{ClN}^+\cdot\text{C}_7\text{H}_7\text{O}_3\text{S}^-$, the cations and anions are linked *via* $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds into doubled chains in [010]. Weak intermolecular $\text{C}-\text{H}\cdots\pi$ interactions further link these chains into layers parallel to the bc plane.

Related literature

For background to molecular-ionic compounds, see: Czupinski *et al.* (2002); Katrusiak & Szafranski (2006). For related structures, see: Chanawanno *et al.* (2009); Chantrapromma *et al.* (2010); Collier *et al.* (2006); Fun *et al.* (2010); Li *et al.* (2005); Lin (2010); Tabatabaee & Noozari (2011); Wu *et al.* (2009). For normal bond lengths in organic compounds, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_6\text{H}_7\text{ClN}^+\cdot\text{C}_7\text{H}_7\text{O}_3\text{S}^-$
 $M_r = 299.76$
 Monoclinic, $P2_1/c$
 $a = 12.7848$ (3) Å
 $b = 6.7767$ (2) Å
 $c = 16.1702$ (4) Å
 $\beta = 105.081$ (2)°

$V = 1352.71$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.44$ mm⁻¹
 $T = 298$ K
 $0.32 \times 0.26 \times 0.20$ mm

Data collection

Oxford Diffraction Xcalibur Eos
 Gemini diffractometer
 Absorption correction: multi-scan
 (*CrysAlis RED*; Oxford
 Diffraction, 2010)
 $T_{\min} = 0.872$, $T_{\max} = 0.917$

10965 measured reflections
 3222 independent reflections
 2723 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.109$
 $S = 1.02$
 3222 reflections
 182 parameters
 6 restraints

H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.47$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1–C6 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1NA}\cdots\text{O1}^{\text{i}}$	0.92 (1)	1.86 (1)	2.7640 (19)	168 (2)
$\text{N1}-\text{H1NC}\cdots\text{O3}^{\text{ii}}$	0.93 (1)	1.87 (1)	2.7806 (18)	166 (2)
$\text{N1}-\text{H1NB}\cdots\text{O2}$	0.93 (1)	1.92 (1)	2.8282 (19)	167 (2)
$\text{C12}-\text{H12A}\cdots\text{Cg1}^{\text{iii}}$	0.93	2.76	3.267 (2)	115

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

ASP and HSY thank the UoM for research facilities. JPJ acknowledges the NSF-MRI program (grant No. CHE1039027) for funds to purchase the X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5151).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Chanawanno, K., Chantrapromma, S. & Fun, H.-K. (2009). *Anal. Sci.* **25**, 127–128.
- Chantrapromma, S., Chanawanno, K. & Fun, H.-K. (2010). *Acta Cryst.* **E66**, o1975–o1976.
- Collier, E. A., Davey, R. J., Black, S. N. & Roberts, R. J. (2006). *Acta Cryst.* **B62**, 498–505.
- Czupinski, O., Bator, G., Ciunik, Z., Jakubas, R., Medycki, W. & Swiergiel, J. (2002). *J. Phys. Condens. Matter*, **14**, 8497–8512.
- Fun, H.-K., Kobkeatthawin, T. & Chantrapromma, S. (2010). *Acta Cryst.* **E66**, o1053–o1054.
- Katrusiak, A. & Szafranski, M. (2006). *J. Am. Chem. Soc.* **128**, 15775–15785.
- Li, X.-M., Lu, L.-P., Feng, S.-S., Zhang, H.-M., Qin, S.-D. & Zhu, M.-L. (2005). *Acta Cryst.* **E61**, o811–o813.
- Lin, J. R. (2010). *Acta Cryst.* **E66**, o1557.
- Oxford Diffraction (2010). *CrysAlis PRO* and *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, England.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Tabatabaee, M. & Noozari, N. (2011). *Acta Cryst.* **E67**, o1457.
- Wu, T.-Q., Xia, L., Hu, A.-X. & Ye, J. (2009). *Acta Cryst.* **E65**, o368.

supporting information

Acta Cryst. (2011). E67, o2925 [doi:10.1107/S1600536811041043]

3-Chloroanilinium 4-methylbenzenesulfonate

Jerry P. Jasinski, James A. Golen, A. S. Praveen, H. S. Yathirajan and B. Narayana

S1. Comment

Recently much attention has been devoted to simple molecular-ionic crystals containing organic cations and anions due to the tunability of their special structural features and their interesting physical properties (Czupinski *et al.*, 2002; Katrusiak & Szafranski, 2006). A variety of pharmaceutical drugs are prepared as salts of benzenesulfonic acid and are known as besylates. Crystal structures of some benzenesulfonate derivatives, viz., 2,4,6-triamino-1,3,5-triazin-1-ium 4-methylbenzenesulfonate monohydrate (Li *et al.*, 2005), ephedrine besylate (Collier *et al.*, 2006), 2-ethyl-6-methyl-anilinium 4-methylbenzenesulfonate (Wu *et al.*, 2009), 2-[(E)-2-(4-ethoxyphenyl)ethenyl]-1-methylpyridinium 4-methylbenzenesulfonate monohydrate (Chanawanno *et al.*, 2009), 2-aminopyrimidin-1-ium 4-methylbenzenesulfonate (Tabatabaee & Noozari, 2011), 4-(cyanomethyl)anilinium 4-methylbenzenesulfonate monohydrate (Lin, 2010), 1-methyl-2-[(E)-2-(2-thienyl)ethenyl] quinolinium 4-bromobenzenesulfonate (Fun *et al.*, 2010) and (E)-2-[4-(dimethyl-amino)styryl]-1-methylpyridinium 4-methylbenzenesulfonate monohydrate (Chantrapromma *et al.*, 2010) have been reported. In view of the importance of benzenesulphonic acid, we report herein the crystal structure of the title compound (I).

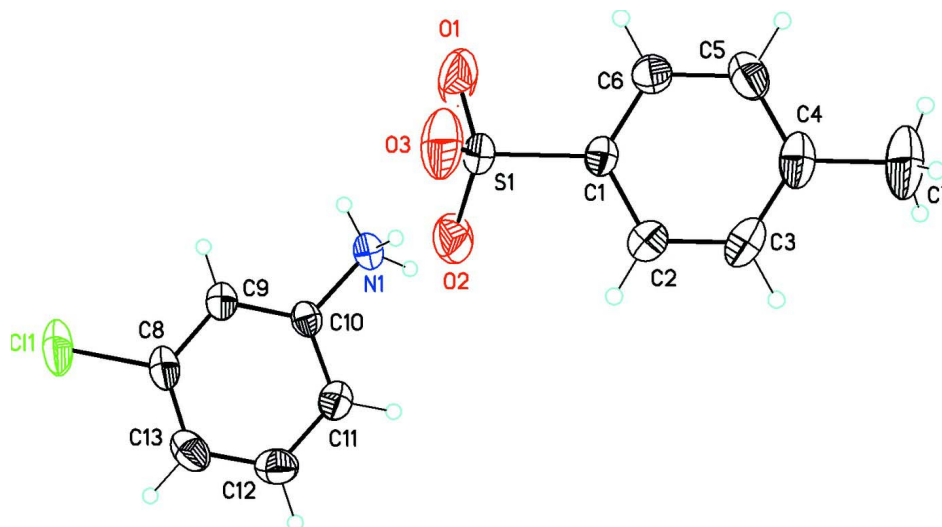
In the crystal structure of the title salt, $C_6H_7ClN^+ \cdot C_7H_7O_3S^-$ (Fig. 1), the cations and anions are linked *via* N—H \cdots O hydrogen bonds into doubled chains in [010]. Weak intermolecular C—H \cdots π interactions (Table 1) link further these chains into layers parallel to the *bc* plane.

S2. Experimental

To a stirred solution of 3-chloroaniline (0.67 g, 5.25 mmol) in methanol (15 ml), 4-methylbenzenesulfonic acid monohydrate (1g, 5.25 mmol) was added, stirred at 323 K for 10 minutes and cooled to room temperature to afford the title compound (I). The single crystal was grown from methanol by slow evaporation method (M.P.: 538-540 K).

S3. Refinement

H1NA, H1NB and H1NC were located on a Fourier map and refined isotropically. All of the remaining H atoms were placed in their calculated positions and then refined using the riding model with C—H bond lengths of 0.93 Å (CH) or 0.96 Å (CH₃). Isotropic displacement parameters for these atoms were set to 1.18-1.20 (CH) or 1.49 (CH₃) times U_{eq} of the parent atom.

**Figure 1**

Molecular structure of the title compound showing the atom labeling scheme and 30% probability displacement ellipsoids.

3-Chloroanilinium 4-methylbenzenesulfonate

Crystal data

$C_6H_7ClN^+ \cdot C_7H_7O_3S^-$

$M_r = 299.76$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 12.7848\ (3)\ \text{\AA}$

$b = 6.7767\ (2)\ \text{\AA}$

$c = 16.1702\ (4)\ \text{\AA}$

$\beta = 105.081\ (2)^\circ$

$V = 1352.71\ (6)\ \text{\AA}^3$

$Z = 4$

$F(000) = 624$

$D_x = 1.472\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4281 reflections

$\theta = 3.2\text{--}30.0^\circ$

$\mu = 0.44\ \text{mm}^{-1}$

$T = 298\ \text{K}$

Block, colourless

$0.32 \times 0.26 \times 0.20\ \text{mm}$

Data collection

Oxford Diffraction Xcalibur Eos Gemini diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: $16.1500\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan

(*CrysAlis RED*; Oxford Diffraction, 2010)

$T_{\min} = 0.872$, $T_{\max} = 0.917$

10965 measured reflections

3222 independent reflections

2723 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 27.9^\circ$, $\theta_{\min} = 3.3^\circ$

$h = -16 \rightarrow 16$

$k = -8 \rightarrow 8$

$l = -21 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.109$

$S = 1.02$

3222 reflections

182 parameters

6 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.4988P]$
where $P = (F_o^2 + 2F_c^2)/3$

$$\begin{aligned}(\Delta/\sigma)_{\max} &= 0.016 \\ \Delta\rho_{\max} &= 0.38 \text{ e } \text{\AA}^{-3} \\ \Delta\rho_{\min} &= -0.47 \text{ e } \text{\AA}^{-3}\end{aligned}$$

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.

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.71334 (3)	0.24308 (5)	0.57609 (2)	0.03033 (13)
Cl1	0.48393 (5)	0.72176 (8)	0.12500 (3)	0.05637 (17)
O1	0.60656 (10)	0.2751 (3)	0.58758 (10)	0.0679 (5)
O2	0.74597 (11)	0.4022 (2)	0.52892 (8)	0.0533 (4)
O3	0.72546 (12)	0.0520 (2)	0.54113 (9)	0.0589 (4)
N1	0.61726 (11)	0.7273 (2)	0.45378 (9)	0.0314 (3)
H1NC	0.6457 (12)	0.8338 (18)	0.4885 (10)	0.038*
H1NB	0.6507 (12)	0.6166 (17)	0.4825 (10)	0.038*
H1NA	0.5440 (7)	0.721 (2)	0.4477 (12)	0.038*
C1	0.80291 (12)	0.2481 (2)	0.67983 (10)	0.0277 (3)
C2	0.90883 (13)	0.3131 (2)	0.69108 (11)	0.0345 (3)
H2A	0.9330	0.3532	0.6442	0.041*
C3	0.97806 (13)	0.3175 (3)	0.77261 (12)	0.0403 (4)
H3A	1.0489	0.3612	0.7800	0.048*
C4	0.94414 (16)	0.2583 (2)	0.84357 (12)	0.0421 (4)
C5	0.83782 (16)	0.1937 (3)	0.83099 (11)	0.0430 (4)
H5A	0.8137	0.1532	0.8778	0.052*
C6	0.76757 (14)	0.1887 (2)	0.74998 (10)	0.0356 (3)
H6A	0.6967	0.1456	0.7426	0.043*
C7	1.0204 (2)	0.2665 (3)	0.93256 (15)	0.0687 (7)
H7A	1.0613	0.3869	0.9391	0.103*
H7B	1.0690	0.1560	0.9406	0.103*
H7C	0.9792	0.2618	0.9744	0.103*
C8	0.58589 (15)	0.7473 (2)	0.21912 (10)	0.0347 (4)
C9	0.56033 (13)	0.7206 (2)	0.29641 (10)	0.0312 (3)
H9A	0.4907	0.6851	0.2983	0.037*
C10	0.64148 (12)	0.7483 (2)	0.37058 (10)	0.0271 (3)
C11	0.74566 (13)	0.7990 (2)	0.36897 (11)	0.0348 (3)
H11A	0.7992	0.8178	0.4196	0.042*
C12	0.76860 (15)	0.8212 (3)	0.29072 (12)	0.0412 (4)
H12A	0.8387	0.8532	0.2888	0.049*

C13	0.68918 (16)	0.7965 (2)	0.21532 (11)	0.0414 (4)
H13A	0.7050	0.8128	0.1628	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0291 (2)	0.0332 (2)	0.0253 (2)	0.00048 (14)	0.00097 (14)	-0.00304 (13)
Cl1	0.0735 (4)	0.0580 (3)	0.0257 (2)	-0.0038 (2)	-0.0086 (2)	-0.00145 (18)
O1	0.0290 (7)	0.1261 (15)	0.0437 (8)	0.0078 (7)	0.0005 (6)	-0.0142 (8)
O2	0.0579 (8)	0.0538 (8)	0.0393 (7)	-0.0066 (6)	-0.0031 (6)	0.0160 (6)
O3	0.0771 (10)	0.0408 (7)	0.0450 (8)	0.0047 (7)	-0.0089 (7)	-0.0176 (6)
N1	0.0340 (7)	0.0355 (7)	0.0231 (6)	0.0001 (5)	0.0046 (5)	-0.0005 (5)
C1	0.0287 (7)	0.0251 (7)	0.0262 (7)	0.0009 (5)	0.0019 (6)	-0.0020 (5)
C2	0.0303 (8)	0.0347 (8)	0.0374 (8)	-0.0004 (6)	0.0068 (6)	-0.0022 (7)
C3	0.0297 (8)	0.0361 (8)	0.0480 (10)	0.0004 (7)	-0.0026 (7)	-0.0085 (7)
C4	0.0492 (10)	0.0313 (8)	0.0356 (9)	0.0063 (7)	-0.0073 (8)	-0.0051 (6)
C5	0.0594 (11)	0.0369 (9)	0.0302 (8)	-0.0026 (8)	0.0074 (8)	0.0037 (7)
C6	0.0378 (8)	0.0322 (8)	0.0353 (8)	-0.0061 (7)	0.0072 (7)	0.0015 (6)
C7	0.0792 (16)	0.0634 (14)	0.0436 (13)	0.0091 (11)	-0.0198 (11)	-0.0108 (9)
C8	0.0475 (9)	0.0283 (8)	0.0236 (7)	0.0016 (7)	0.0009 (6)	-0.0006 (5)
C9	0.0342 (8)	0.0300 (8)	0.0267 (7)	0.0002 (6)	0.0031 (6)	-0.0010 (6)
C10	0.0325 (7)	0.0239 (7)	0.0236 (7)	0.0025 (5)	0.0052 (6)	0.0008 (5)
C11	0.0345 (8)	0.0342 (8)	0.0329 (8)	-0.0021 (6)	0.0035 (6)	-0.0020 (6)
C12	0.0419 (9)	0.0392 (9)	0.0467 (10)	-0.0064 (7)	0.0189 (8)	-0.0009 (8)
C13	0.0625 (11)	0.0333 (8)	0.0320 (8)	-0.0050 (8)	0.0187 (8)	0.0015 (7)

Geometric parameters (Å, °)

S1—O3	1.4374 (13)	C5—C6	1.382 (2)
S1—O2	1.4437 (13)	C5—H5A	0.9300
S1—O1	1.4413 (14)	C6—H6A	0.9300
S1—C1	1.7682 (15)	C7—H7A	0.9600
Cl1—C8	1.7359 (17)	C7—H7B	0.9600
N1—C10	1.464 (2)	C7—H7C	0.9600
N1—H1NC	0.928 (9)	C8—C9	1.383 (2)
N1—H1NB	0.927 (8)	C8—C13	1.379 (3)
N1—H1NA	0.916 (9)	C9—C10	1.379 (2)
C1—C6	1.386 (2)	C9—H9A	0.9300
C1—C2	1.390 (2)	C10—C11	1.382 (2)
C2—C3	1.384 (2)	C11—C12	1.379 (2)
C2—H2A	0.9300	C11—H11A	0.9300
C3—C4	1.387 (3)	C12—C13	1.379 (3)
C3—H3A	0.9300	C12—H12A	0.9300
C4—C5	1.392 (3)	C13—H13A	0.9300
C4—C7	1.515 (3)		
O3—S1—O2	112.92 (9)	C1—C6—C5	119.92 (16)
O3—S1—O1	112.90 (10)	C1—C6—H6A	120.0

O2—S1—O1	111.66 (10)	C5—C6—H6A	120.0
O3—S1—C1	106.32 (7)	C4—C7—H7A	109.5
O2—S1—C1	106.38 (7)	C4—C7—H7B	109.5
O1—S1—C1	106.03 (8)	H7A—C7—H7B	109.5
C10—N1—H1NC	109.7 (11)	C4—C7—H7C	109.5
C10—N1—H1NB	111.1 (11)	H7A—C7—H7C	109.5
H1NC—N1—H1NB	105.6 (14)	H7B—C7—H7C	109.5
C10—N1—H1NA	111.2 (12)	C9—C8—C13	121.74 (16)
H1NC—N1—H1NA	109.0 (13)	C9—C8—C11	118.62 (14)
H1NB—N1—H1NA	110.1 (13)	C13—C8—C11	119.64 (13)
C6—C1—C2	119.93 (14)	C10—C9—C8	117.81 (15)
C6—C1—S1	120.17 (12)	C10—C9—H9A	121.1
C2—C1—S1	119.91 (12)	C8—C9—H9A	121.1
C3—C2—C1	119.43 (16)	C9—C10—C11	121.86 (14)
C3—C2—H2A	120.3	C9—C10—N1	119.65 (14)
C1—C2—H2A	120.3	C11—C10—N1	118.47 (13)
C2—C3—C4	121.43 (16)	C12—C11—C10	118.70 (15)
C2—C3—H3A	119.3	C12—C11—H11A	120.7
C4—C3—H3A	119.3	C10—C11—H11A	120.7
C3—C4—C5	118.27 (16)	C13—C12—C11	120.97 (16)
C3—C4—C7	120.85 (19)	C13—C12—H12A	119.5
C5—C4—C7	120.9 (2)	C11—C12—H12A	119.5
C6—C5—C4	121.02 (17)	C12—C13—C8	118.91 (16)
C6—C5—H5A	119.5	C12—C13—H13A	120.5
C4—C5—H5A	119.5	C8—C13—H13A	120.5
O3—S1—C1—C6	-90.75 (15)	C2—C1—C6—C5	-0.2 (2)
O2—S1—C1—C6	148.65 (13)	S1—C1—C6—C5	-179.74 (13)
O1—S1—C1—C6	29.65 (16)	C4—C5—C6—C1	0.2 (3)
O3—S1—C1—C2	89.72 (14)	C13—C8—C9—C10	1.2 (2)
O2—S1—C1—C2	-30.89 (15)	C11—C8—C9—C10	-177.74 (11)
O1—S1—C1—C2	-149.88 (14)	C8—C9—C10—C11	-0.7 (2)
C6—C1—C2—C3	0.1 (2)	C8—C9—C10—N1	178.21 (13)
S1—C1—C2—C3	179.61 (12)	C9—C10—C11—C12	-0.4 (2)
C1—C2—C3—C4	0.1 (3)	N1—C10—C11—C12	-179.27 (15)
C2—C3—C4—C5	-0.1 (3)	C10—C11—C12—C13	1.0 (3)
C2—C3—C4—C7	-179.20 (16)	C11—C12—C13—C8	-0.6 (3)
C3—C4—C5—C6	-0.1 (3)	C9—C8—C13—C12	-0.5 (2)
C7—C4—C5—C6	179.06 (17)	C11—C8—C13—C12	178.34 (13)

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

Cg1 is the centroid of the C1—C6 ring.

<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—H1NA \cdots O1 ⁱ	0.92 (1)	1.86 (1)	2.7640 (19)	168 (2)
N1—H1NC \cdots O3 ⁱⁱ	0.93 (1)	1.87 (1)	2.7806 (18)	166 (2)

N1—H1 <i>N</i> B···O2	0.93 (1)	1.92 (1)	2.8282 (19)	167 (2)
C12—H12 <i>A</i> ···Cg1 ⁱⁱⁱ	0.93	2.76	3.267 (2)	115

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