

# Crystal structure of 4,4'-(ethene-1,2-diyl)dipyridinium bis(3-carboxybenzenesulfonate)

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Received 8 October 2014; accepted 15 October 2014

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

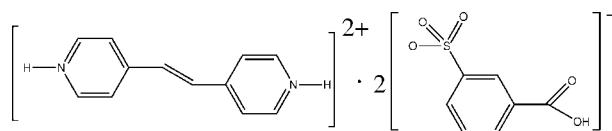
In the title molecular salt,  $C_{12}H_{12}N_2^{2+} \cdot 2C_7H_5O_5S^-$ , the complete dication is generated by crystallographic inversion symmetry. In the anion, the sulfonic acid group is deprotonated and the dihedral angle between the planes of the carboxylic acid group and the benzene ring is  $12.41(11)^\circ$ . In the crystal, the anions are linked into inversion dimers by pairs of  $O-H \cdots O$  hydrogen bonds, which generate  $R_2^2(16)$  loops. The dications link the anion dimers into  $[10\bar{2}]$  chains *via*  $N-H \cdots O$  hydrogen bonds.

**Keywords:** crystal structure; 3-sulfobenzoate; 1,2-bis(pyridin-4-yl)ethylene; hydrogen bonding; 4,4'-(ethane-1,2-diyl)dipyridinium.

**CCDC reference:** 1029402

## 1. Related literature

For general background to salts of 1,2-bis(pyridin-4-yl)ethylene and sulfobenzoates and their applications, see: Ma & Zhu (2014); Zheng & Zhu (2014); Lesniewska *et al.* (2014); Danylyuk *et al.* (2010); Zhang & Zhu (2006, 2007).



## 2. Experimental

### 2.1. Crystal data

$C_{12}H_{12}N_2^{2+} \cdot 2C_7H_5O_5S^-$   
 $M_r = 586.58$   
 Triclinic,  $P\bar{1}$   
 $a = 7.4573(5) \text{ \AA}$   
 $b = 7.8381(6) \text{ \AA}$   
 $c = 11.3111(9) \text{ \AA}$   
 $\alpha = 85.525(6)^\circ$   
 $\beta = 86.634(6)^\circ$

$\gamma = 69.545(7)^\circ$   
 $V = 617.22(8) \text{ \AA}^3$   
 $Z = 1$   
 Mo  $K\alpha$  radiation

$\mu = 0.28 \text{ mm}^{-1}$   
 $T = 170 \text{ K}$   
 $0.43 \times 0.29 \times 0.18 \text{ mm}$

### 2.2. Data collection

Oxford Diffraction Xcalibur (Atlas, Gemini Ultra CCD) diffractometer  
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)  
 $T_{\min} = 0.888$ ,  $T_{\max} = 0.951$   
 3834 measured reflections  
 2182 independent reflections  
 1899 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.096$   
 $S = 0.98$   
 2182 reflections  
 187 parameters  
 2 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$

**Table 1**

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O5-H5A \cdots O3^i$	0.86 (1)	1.85 (1)	2.683 (2)	163 (3)
$N1-H1A \cdots O1^{ii}$	0.83 (1)	1.91 (1)	2.727 (2)	172 (4)

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

## Acknowledgements

We acknowledge support from the National Natural Science Foundation of China (grant No. 21073157).

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7296).

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## supporting information

*Acta Cryst.* (2014). E70, o1170 [doi:10.1107/S1600536814022673]

## Crystal structure of 4,4'-(ethene-1,2-diyl)dipyridinium bis(3-carboxybenzenesulfonate)

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### S1. Comment

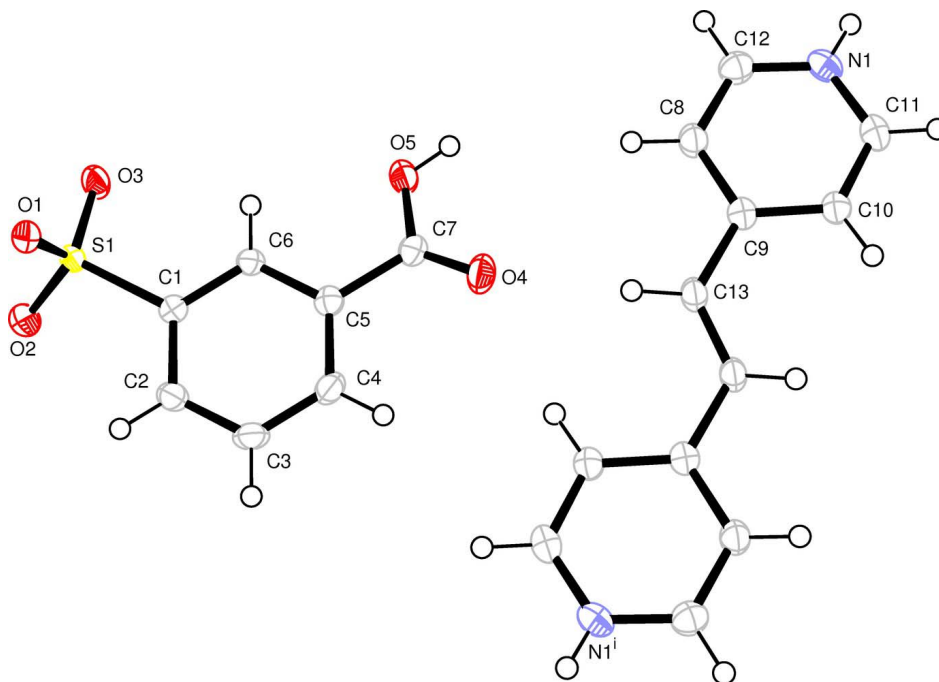
Sulfobenzoate derivatives and their organic or coordination compounds are very interesting in material science, such as potential applications in fluorescence and catalytic fields (Ma & Zhu, 2014; Zheng & Zhu, 2014). Sulfobenzoates have two functional groups, sulfonate and carboxylate, and can coordinate to metal ions *via* versatile coordination modes or can form abundant hydrogen bonds due to they have five donors or acceptors. The 1,2-bis(pyridin-4-yl)ethylene derivatives have been widely used as bridge linkers in the coordination chemistry. several organic complexes with the 1,2-bis(pyridin-4-yl)ethylene and sulfobenzoate ligands have been reported, such as, 4,4'-ethylene-1,2-diyl dipyridinium bis(4-carboxybenzenesulfonate) dihydrate (Zheng & Zhu, 2014), bis(4-(2-(pyridin-4-yl)vinyl)pyridinium) 4-sulfonato-benzoate trihydrate (Zhang & Zhu, 2006), and 4-(2-(pyridin-4-yl)ethenyl)pyridinium 2-carboxybenzenesulfonate (Zhang & Zhu, 2007). The title compound has 1:2 ratio of cation to anion without any water molecule (Fig. 1). The cation is protonated and the anion is partly deprotonated. Two pyridyl rings of the 4-(2-(pyridin-4-yl)ethenyl)pyridinium anion are coplanar and the whole cation is a big pi-conjugated system. Two anions are linked by O—H $\cdots$ O between sulfonate and carboxylate groups into a dimer and these anionic dimers interact with cations by N—H $\cdots$ O hydrogen bonds, generating a chain (Fig. 2).

### S2. Experimental

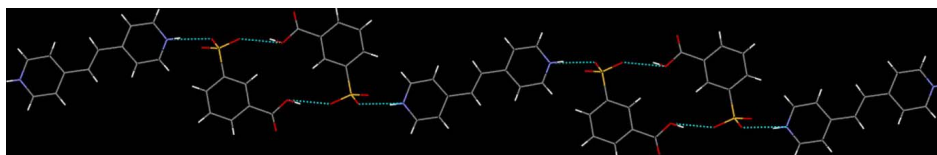
A mixed solution of 3-sulfobenzoate sodium (0.224 g, 1 mmol) in 10 ml CH<sub>3</sub>OH and 1,2-bis(pyridin-4-yl)ethylene (0.091 g, 0.5 mmol) in 8 ml of CH<sub>3</sub>CN was stirred for one hour and set aside for slow evaporation at room temperature. After two days, yellow plates were obtained and collected by filtration.

### S3. Refinement

The nitrogen and carboxylate H atoms were found in the Fourier map with fixed  $U_{\text{iso}}=0.08 \text{ \AA}^2$ . The other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of C—H=0.93 Å (for  $C_{sp^2}$ ) with  $U_{\text{iso}}=1.2U_{\text{eq}}$ (parent atom).

**Figure 1**

View of the asymmetry unit of (I) showing displacement ellipsoids at the 50% probability level. Symmetry code: (i)  $2-x, -y, 1-z$ .

**Figure 2**

The hydrogen-bonded chain of (I).

#### 4,4'-(Ethene-1,2-diyl)dipyridinium bis(3-carboxybenzenesulfonate)

##### Crystal data

$C_{12}H_{12}N_2^{2+} \cdot 2C_7H_5O_5S^-$

$M_r = 586.58$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 7.4573$  (5) Å

$b = 7.8381$  (6) Å

$c = 11.3111$  (9) Å

$\alpha = 85.525$  (6)°

$\beta = 86.634$  (6)°

$\gamma = 69.545$  (7)°

$V = 617.22$  (8) Å<sup>3</sup>

$Z = 1$

$F(000) = 304$

$D_x = 1.578$  Mg m<sup>-3</sup>

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

Cell parameters from 1621 reflections

$\theta = 3.3$ – $29.4$ °

$\mu = 0.28$  mm<sup>-1</sup>

$T = 170$  K

Plate, yellow

$0.43 \times 0.29 \times 0.18$  mm

*Data collection*

Oxford Diffraction Xcalibur (Atlas, Gemini Ultra CCD) diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\omega$  scans  
 Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)  
 $T_{\min} = 0.888$ ,  $T_{\max} = 0.951$

3834 measured reflections  
 2182 independent reflections  
 1899 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$   
 $\theta_{\max} = 25.1^\circ$ ,  $\theta_{\min} = 3.3^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -8 \rightarrow 9$   
 $l = -13 \rightarrow 11$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.096$   
 $S = 0.98$   
 2182 reflections  
 187 parameters  
 2 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 0.4291P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$

*Special details*

**Experimental.** Absorption correction: CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.53 (release 17-11-2009 CrysAlis171 .NET) (compiled Nov 17 2009,16:58:22) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

**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  $F^2 > \sigma(F^2)$  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>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.19563 (7)	1.18509 (7)	0.82396 (4)	0.02058 (17)
N1	1.2183 (2)	0.1796 (3)	0.13817 (15)	0.0249 (4)
H1A	1.254 (5)	0.198 (5)	0.0693 (13)	0.080*
O1	0.3295 (2)	1.2088 (2)	0.90567 (12)	0.0262 (3)
O2	0.0064 (2)	1.2254 (2)	0.87794 (13)	0.0297 (4)
O3	0.1989 (2)	1.2820 (2)	0.70976 (13)	0.0309 (4)
O4	0.6933 (2)	0.4749 (2)	0.56362 (13)	0.0313 (4)
O5	0.5777 (2)	0.7626 (2)	0.48846 (14)	0.0339 (4)
H5A	0.656 (4)	0.725 (5)	0.430 (2)	0.080*
C1	0.2852 (3)	0.9481 (3)	0.79837 (17)	0.0197 (4)
C2	0.2567 (3)	0.8244 (3)	0.88595 (18)	0.0242 (5)
H2	0.1840	0.8660	0.9543	0.029*

C3	0.3371 (3)	0.6395 (3)	0.87079 (19)	0.0271 (5)
H3	0.3179	0.5567	0.9291	0.032*
C4	0.4461 (3)	0.5766 (3)	0.76930 (19)	0.0258 (5)
H4	0.5019	0.4519	0.7603	0.031*
C5	0.4716 (3)	0.7008 (3)	0.68091 (17)	0.0206 (4)
C6	0.3908 (3)	0.8874 (3)	0.69538 (17)	0.0196 (4)
H6	0.4076	0.9706	0.6364	0.024*
C7	0.5925 (3)	0.6311 (3)	0.57261 (18)	0.0231 (5)
C8	1.0500 (3)	0.2889 (3)	0.31413 (18)	0.0246 (5)
H8	0.9812	0.3866	0.3592	0.029*
C9	1.0830 (3)	0.1109 (3)	0.36022 (17)	0.0204 (4)
C10	1.1909 (3)	-0.0318 (3)	0.29100 (18)	0.0233 (5)
H10	1.2187	-0.1522	0.3200	0.028*
C11	1.2553 (3)	0.0070 (3)	0.18050 (18)	0.0255 (5)
H11	1.3260	-0.0879	0.1338	0.031*
C12	1.1187 (3)	0.3205 (3)	0.20264 (19)	0.0269 (5)
H12	1.0961	0.4394	0.1719	0.032*
C13	1.0020 (3)	0.0799 (3)	0.47750 (18)	0.0228 (4)
H13	0.9494	0.1797	0.5238	0.027*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0253 (3)	0.0180 (3)	0.0175 (3)	-0.0069 (2)	0.00549 (19)	-0.0025 (2)
N1	0.0229 (9)	0.0334 (11)	0.0187 (9)	-0.0105 (8)	0.0001 (7)	-0.0006 (8)
O1	0.0315 (8)	0.0256 (8)	0.0249 (8)	-0.0138 (6)	0.0056 (6)	-0.0080 (6)
O2	0.0277 (8)	0.0274 (9)	0.0327 (9)	-0.0085 (7)	0.0088 (6)	-0.0058 (7)
O3	0.0460 (9)	0.0195 (8)	0.0206 (8)	-0.0048 (7)	0.0085 (6)	-0.0004 (6)
O4	0.0364 (9)	0.0205 (8)	0.0320 (9)	-0.0030 (7)	0.0022 (6)	-0.0070 (7)
O5	0.0473 (10)	0.0223 (8)	0.0260 (9)	-0.0066 (7)	0.0134 (7)	-0.0033 (7)
C1	0.0201 (10)	0.0190 (10)	0.0202 (10)	-0.0071 (8)	-0.0011 (7)	-0.0009 (8)
C2	0.0275 (11)	0.0283 (12)	0.0199 (11)	-0.0139 (9)	0.0025 (8)	-0.0023 (9)
C3	0.0338 (12)	0.0255 (12)	0.0248 (11)	-0.0153 (9)	0.0001 (9)	0.0047 (9)
C4	0.0311 (12)	0.0181 (11)	0.0291 (12)	-0.0094 (9)	-0.0012 (9)	-0.0030 (9)
C5	0.0199 (10)	0.0221 (11)	0.0211 (11)	-0.0084 (8)	-0.0025 (8)	-0.0025 (8)
C6	0.0224 (10)	0.0199 (11)	0.0180 (10)	-0.0091 (8)	0.0004 (8)	-0.0008 (8)
C7	0.0259 (11)	0.0218 (11)	0.0232 (11)	-0.0098 (9)	-0.0007 (8)	-0.0042 (9)
C8	0.0271 (11)	0.0228 (11)	0.0222 (11)	-0.0063 (9)	0.0012 (8)	-0.0042 (9)
C9	0.0177 (10)	0.0222 (11)	0.0205 (10)	-0.0056 (8)	-0.0024 (7)	-0.0029 (8)
C10	0.0233 (11)	0.0215 (11)	0.0235 (11)	-0.0059 (8)	0.0016 (8)	-0.0027 (9)
C11	0.0226 (11)	0.0289 (12)	0.0238 (11)	-0.0067 (9)	0.0013 (8)	-0.0074 (9)
C12	0.0269 (11)	0.0253 (12)	0.0282 (12)	-0.0089 (9)	-0.0030 (9)	0.0015 (9)
C13	0.0240 (11)	0.0213 (10)	0.0212 (11)	-0.0048 (8)	0.0025 (8)	-0.0060 (8)

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

S1—O2	1.4426 (15)	C4—C5	1.392 (3)
S1—O3	1.4499 (15)	C4—H4	0.9300

S1—O1	1.4664 (15)	C5—C6	1.393 (3)
S1—C1	1.781 (2)	C5—C7	1.497 (3)
N1—C11	1.338 (3)	C6—H6	0.9300
N1—C12	1.339 (3)	C8—C12	1.370 (3)
N1—H1A	0.827 (10)	C8—C9	1.392 (3)
O4—C7	1.200 (3)	C8—H8	0.9300
O5—C7	1.327 (3)	C9—C10	1.395 (3)
O5—H5A	0.855 (10)	C9—C13	1.464 (3)
C1—C6	1.386 (3)	C10—C11	1.363 (3)
C1—C2	1.392 (3)	C10—H10	0.9300
C2—C3	1.381 (3)	C11—H11	0.9300
C2—H2	0.9300	C12—H12	0.9300
C3—C4	1.386 (3)	C13—C13 <sup>i</sup>	1.324 (4)
C3—H3	0.9300	C13—H13	0.9300
O2—S1—O3	113.77 (9)	C1—C6—C5	119.45 (18)
O2—S1—O1	111.53 (9)	C1—C6—H6	120.3
O3—S1—O1	112.10 (9)	C5—C6—H6	120.3
O2—S1—C1	107.31 (9)	O4—C7—O5	123.92 (19)
O3—S1—C1	106.65 (9)	O4—C7—C5	123.93 (19)
O1—S1—C1	104.84 (9)	O5—C7—C5	112.14 (17)
C11—N1—C12	121.56 (18)	C12—C8—C9	120.2 (2)
C11—N1—H1A	118 (3)	C12—C8—H8	119.9
C12—N1—H1A	120 (3)	C9—C8—H8	119.9
C7—O5—H5A	112 (2)	C8—C9—C10	118.08 (18)
C6—C1—C2	120.52 (19)	C8—C9—C13	119.46 (18)
C6—C1—S1	120.31 (15)	C10—C9—C13	122.45 (19)
C2—C1—S1	119.08 (15)	C11—C10—C9	119.4 (2)
C3—C2—C1	119.64 (19)	C11—C10—H10	120.3
C3—C2—H2	120.2	C9—C10—H10	120.3
C1—C2—H2	120.2	N1—C11—C10	121.0 (2)
C2—C3—C4	120.50 (19)	N1—C11—H11	119.5
C2—C3—H3	119.7	C10—C11—H11	119.5
C4—C3—H3	119.7	N1—C12—C8	119.7 (2)
C3—C4—C5	119.72 (19)	N1—C12—H12	120.1
C3—C4—H4	120.1	C8—C12—H12	120.1
C5—C4—H4	120.1	C13 <sup>i</sup> —C13—C9	124.8 (2)
C4—C5—C6	120.14 (18)	C13 <sup>i</sup> —C13—H13	117.6
C4—C5—C7	119.23 (18)	C9—C13—H13	117.6
C6—C5—C7	120.59 (18)		
O2—S1—C1—C6	140.83 (16)	C7—C5—C6—C1	-177.69 (17)
O3—S1—C1—C6	18.56 (18)	C4—C5—C7—O4	-11.6 (3)
O1—S1—C1—C6	-100.47 (16)	C6—C5—C7—O4	166.22 (19)
O2—S1—C1—C2	-42.65 (18)	C4—C5—C7—O5	169.47 (18)
O3—S1—C1—C2	-164.92 (15)	C6—C5—C7—O5	-12.7 (3)
O1—S1—C1—C2	76.05 (17)	C12—C8—C9—C10	1.6 (3)
C6—C1—C2—C3	1.1 (3)	C12—C8—C9—C13	-177.52 (19)

S1—C1—C2—C3	-175.44 (15)	C8—C9—C10—C11	-1.8 (3)
C1—C2—C3—C4	0.2 (3)	C13—C9—C10—C11	177.25 (18)
C2—C3—C4—C5	-1.3 (3)	C12—N1—C11—C10	0.6 (3)
C3—C4—C5—C6	1.1 (3)	C9—C10—C11—N1	0.8 (3)
C3—C4—C5—C7	178.94 (18)	C11—N1—C12—C8	-0.9 (3)
C2—C1—C6—C5	-1.2 (3)	C9—C8—C12—N1	-0.2 (3)
S1—C1—C6—C5	175.28 (14)	C8—C9—C13—C13 <sup>i</sup>	169.0 (2)
C4—C5—C6—C1	0.1 (3)	C10—C9—C13—C13 <sup>i</sup>	-10.1 (4)

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

*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>
O5—H5A...O3 <sup>ii</sup>	0.86 (1)	1.85 (1)	2.683 (2)	163 (3)
N1—H1A...O1 <sup>iii</sup>	0.83 (1)	1.91 (1)	2.727 (2)	172 (4)

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