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Bis(dimethylammonium) 2,2'-(1,3,6,8-tetraoxo-2,7-diazapyrene-2,7-diyl)-diacetate

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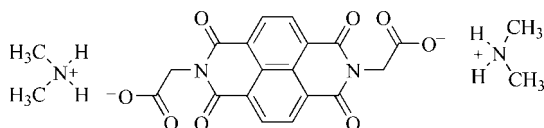
Received 12 June 2011; accepted 4 July 2011

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.040; wR factor = 0.114; data-to-parameter ratio = 11.4.

The asymmetric unit of title compound, $2\text{C}_2\text{H}_8\text{N}^+\cdot\text{C}_{18}\text{H}_8\text{N}_2\text{O}_8^{2-}$, comprises one crystallographically independent dimethylammonium cation and half of a 2,2'-(1,3,6,8-tetraoxo-2,7-diazapyrene-2,7-diyl)diacetate dianion. The anion lies on an inversion centre and the two carboxylate groups are in *trans* positions based on the naphthaleneteracarboxylic diimide group. The crystal packing is stabilized by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds between cations and anions, as well as by $\pi-\pi$ interactions between the naphthaleneteracarboxylic diimide groups [centroid-centroid distance = 4.812 (3) Å].

Related literature

For organic supramolecular solids, see: Pantos *et al.* (2007). For the prediction of organic crystal structures, see: Pigge (2011).



Experimental

Crystal data

 $2\text{C}_2\text{H}_8\text{N}^+\cdot\text{C}_{18}\text{H}_8\text{N}_2\text{O}_8^{2-}$
 $M_r = 472.45$

Triclinic, $P\bar{1}$
 $a = 4.812$ (3) Å
 $b = 8.901$ (5) Å
 $c = 12.640$ (7) Å
 $\alpha = 92.361$ (9)°
 $\beta = 91.512$ (6)°
 $\gamma = 99.789$ (9)°

$V = 532.7$ (5) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 298$ K
 $0.2 \times 0.2 \times 0.2$ mm

Data collection

Rigaku Saturn724+ diffractometer
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku/MS, 2008)
 $T_{\min} = 0.976$, $T_{\max} = 0.983$

4207 measured reflections
 2298 independent reflections
 1969 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.114$
 $S = 1.04$
 2298 reflections

202 parameters
 All H-atom parameters refined
 $\Delta\rho_{\max} = 0.50$ e Å⁻³
 $\Delta\rho_{\min} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H5}\cdots\text{O2}$	1.006 (19)	1.76 (2)	2.7358 (18)	163.5 (16)
$\text{N2}-\text{H6}\cdots\text{O1}^{\text{i}}$	0.94 (2)	2.13 (2)	2.8419 (18)	131.8 (17)
$\text{N2}-\text{H6}\cdots\text{O1}^{\text{ii}}$	0.94 (2)	2.13 (2)	2.935 (2)	142.9 (17)

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

Data collection: *CrystalClear* (Rigaku/MS, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2439).

References

- Pantos, G. D., Wietor, J.-L. & Sanders, J. K. M. (2007). *Angew. Chem. Int. Ed.* **46**, 2238–2240.
 Pigge, F. C. (2011). *CrystEngComm*, **13**, 1733–1748.
 Rigaku/MS (2008). *CrystalClear*. Rigaku/MS Inc., The Woodlands, Texas, USA
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

Acta Cryst. (2011). E67, o1971 [doi:10.1107/S1600536811026511]

Bis(dimethylammonium) 2,2'-(1,3,6,8-tetraoxo-2,7-diazapyrene-2,7-diyl)diacetate

Lan-Ping Xu, Wen-Na Zhao and Lei Han

S1. Comment

The assembly of functionalised organic molecules in the solid state has attracted much attention in crystal engineering and materials science (Pantos *et al.*, 2007). The prediction of organic crystal structures is a central aim of the development of successful synthetic strategies. In general, precise control over solid state assembly processes will facilitate the synthesis of complex functional materials imbued with desirable optical, electronic, magnetic properties starting from carefully chosen yet relatively simple molecular precursors (Pigge, 2011). We are interested in utilizing acid-functionalized naphthalaleneteracarboxylic diimide derivative as starting materials in crystal engineering approaches to a range of functional organic materials. Herein we report an unexpected organic salt compound $2(\text{C}_2\text{H}_8\text{N})\cdot(\text{C}_{18}\text{H}_8\text{N}_2\text{O}_8)$, (**I**), which is prepared under solvothermal reaction from 1,4,5,8-naphthalaleneteracarboxylic diimide-*N,N'*-diacetic acid and 4,4'-bipyridyl in DMF. The dimethylammonium cations come from *in situ* hydrolysis of DMF molecules.

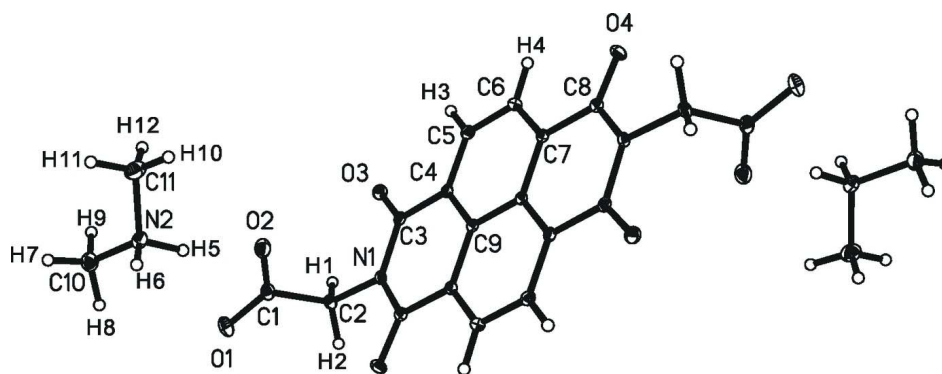
The asymmetric unit of the title compound comprises one crystallographically independent dimethylammonium cation and half of 1,4,5,8-naphthalaleneteracarboxylic diimide-*N,N'*-diacetate anion. As shown in Figure 1, the anion lies on an inversion centre, and the two carboxylate groups of the anion are in *trans* positions based on naphthalaleneteracarboxylic diimide plane. There are strong N—H \cdots O hydrogen bonds between dimethylammonium cations and the carboxylate groups of anions, which are listed in Table 1. The overall hydrogen bonding interaction makes a 12-atom ring and a 4-atom ring, as shown in Figure 2. On the other hand, because of the large π -conjugated skeleton in the naphthalaleneteracarboxylic diimide moiety, the strong intermolecular $\pi\cdots\pi$ interactions are formed with the perpendicular distance between planes of 3.32 Å. Therefore, the crystal packing of **I** is stabilized both by N—H \cdots O hydrogen bonds and $\pi\cdots\pi$ interactions.

S2. Experimental

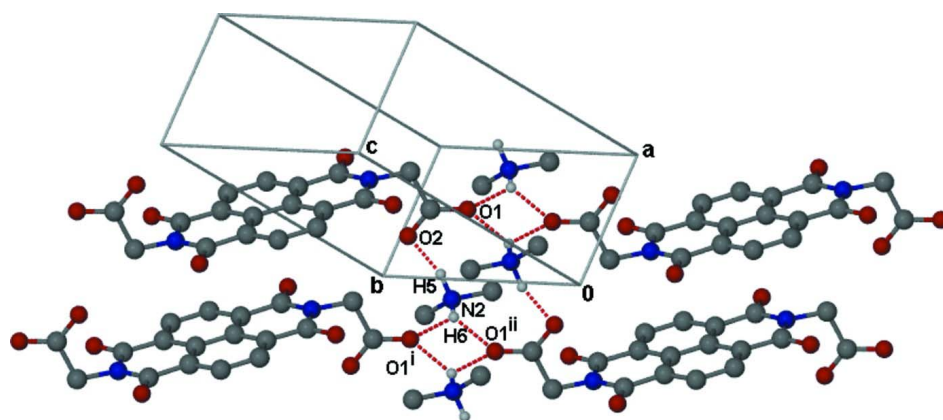
A mixture of 1,4,5,8-naphthalaleneteracarboxylic diimide-*N,N'*-diacetic acid (38.32 mg), 4,4'-bipyridyl (31.24 mg) in DMF (3 ml) was sealed in a 25 ml Teflon-lined stainless steel reactor and heated at 373 K for 72 h. Single crystals of the title compound were obtained after cooling the solution to room temperature, and washed with DMF. The yield is calculated 60%.

S3. Refinement

All H atoms were located in difference maps and refined independently with isotropic displacement parameters.


Figure 1

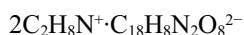
The structure with displacement ellipsoids drawn at the 30% probability level and H atoms shown as small spheres of arbitrary radii.


Figure 2

View of N—H...O hydrogen bonds and $\pi\cdots\pi$ interactions.

Bis(dimethylammonium) 2,2'-(1,3,6,8-tetraoxo-2,7-diazapyrene-2,7-diyl)diacetate

Crystal data



$$M_r = 472.45$$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$$a = 4.812 (3) \text{ \AA}$$

$$b = 8.901 (5) \text{ \AA}$$

$$c = 12.640 (7) \text{ \AA}$$

$$\alpha = 92.361 (9)^\circ$$

$$\beta = 91.512 (6)^\circ$$

$$\gamma = 99.789 (9)^\circ$$

$$V = 532.7 (5) \text{ \AA}^3$$

$$Z = 1$$

$$F(000) = 248$$

$$D_x = 1.473 \text{ Mg m}^{-3}$$

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

Cell parameters from 1620 reflections

$$\theta = 2.3\text{--}27.5^\circ$$

$$\mu = 0.11 \text{ mm}^{-1}$$

$$T = 298 \text{ K}$$

Prism, colorless

$$0.2 \times 0.2 \times 0.2 \text{ mm}$$

Data collection

Rigaku Saturn724+

diffractometer

Radiation source: fine-focus sealed tube

Confocal monochromator

Detector resolution: 28.57 pixels mm^{-1}

ω scans

Absorption correction: multi-scan

(*CrystalClear*; Rigaku/MS, 2008)

$$T_{\min} = 0.976, T_{\max} = 0.983$$

4207 measured reflections

2298 independent reflections
 1969 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.9^\circ$

$h = -6 \rightarrow 6$
 $k = -11 \rightarrow 11$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.114$
 $S = 1.04$
 2298 reflections
 202 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.069P)^2 + 0.126P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.50 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$

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.

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.4577 (2)	0.61234 (11)	0.08100 (7)	0.0248 (3)
O2	0.1971 (2)	0.79037 (11)	0.12376 (7)	0.0252 (3)
O3	0.63240 (19)	1.06673 (10)	0.27584 (7)	0.0179 (2)
O4	-0.2062 (2)	1.40383 (10)	0.63370 (7)	0.0207 (2)
N1	0.4256 (2)	0.83103 (11)	0.32377 (7)	0.0136 (2)
N2	-0.0973 (3)	0.68928 (13)	-0.06090 (8)	0.0204 (3)
H5	0.030 (4)	0.711 (2)	0.0042 (15)	0.038 (5)*
H6	-0.248 (5)	0.615 (2)	-0.0421 (16)	0.046 (6)*
C1	0.3916 (3)	0.71603 (14)	0.14037 (9)	0.0180 (3)
C2	0.5758 (3)	0.75754 (15)	0.24241 (9)	0.0160 (3)
H1	0.736 (4)	0.827 (2)	0.2294 (13)	0.029 (4)*
H2	0.634 (3)	0.6701 (19)	0.2725 (12)	0.022 (4)*
C3	0.4599 (2)	0.99015 (14)	0.32887 (9)	0.0136 (3)
C4	0.2780 (3)	1.06025 (13)	0.40288 (9)	0.0130 (3)
C5	0.2994 (3)	1.21692 (14)	0.41186 (9)	0.0151 (3)
H3	0.429 (4)	1.2802 (18)	0.3699 (13)	0.023 (4)*
C6	0.1307 (3)	1.28406 (14)	0.48269 (9)	0.0159 (3)
H4	0.150 (3)	1.3937 (19)	0.4859 (12)	0.023 (4)*
C7	-0.0576 (3)	1.19431 (13)	0.54381 (9)	0.0131 (3)
C8	-0.2309 (3)	1.26571 (14)	0.62007 (9)	0.0147 (3)
C9	0.0849 (2)	0.96643 (13)	0.46443 (8)	0.0121 (3)

C10	0.0565 (3)	0.62531 (17)	-0.14666 (11)	0.0257 (3)
H7	-0.077 (4)	0.587 (2)	-0.2030 (15)	0.034 (5)*
H8	0.156 (4)	0.544 (2)	-0.1197 (13)	0.030 (4)*
H9	0.190 (4)	0.711 (2)	-0.1699 (15)	0.042 (5)*
C11	-0.1980 (4)	0.83071 (19)	-0.09026 (12)	0.0301 (3)
H12	-0.038 (4)	0.910 (2)	-0.1036 (14)	0.033 (5)*
H11	-0.315 (4)	0.804 (2)	-0.1546 (17)	0.046 (5)*
H10	-0.309 (4)	0.866 (2)	-0.0336 (16)	0.042 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0250 (5)	0.0264 (5)	0.0221 (5)	0.0038 (4)	0.0058 (4)	-0.0082 (4)
O2	0.0258 (5)	0.0310 (6)	0.0201 (5)	0.0102 (4)	-0.0030 (4)	-0.0031 (4)
O3	0.0183 (5)	0.0194 (5)	0.0164 (4)	0.0034 (4)	0.0055 (3)	0.0028 (3)
O4	0.0297 (5)	0.0129 (4)	0.0205 (4)	0.0063 (4)	0.0062 (4)	-0.0011 (3)
N1	0.0163 (5)	0.0152 (5)	0.0102 (5)	0.0054 (4)	0.0016 (4)	-0.0011 (4)
N2	0.0210 (6)	0.0233 (6)	0.0165 (5)	0.0028 (5)	-0.0013 (4)	0.0024 (4)
C1	0.0181 (6)	0.0202 (6)	0.0150 (6)	0.0012 (5)	0.0045 (5)	-0.0003 (4)
C2	0.0177 (6)	0.0174 (6)	0.0144 (5)	0.0071 (5)	0.0042 (5)	-0.0015 (4)
C3	0.0144 (6)	0.0165 (6)	0.0103 (5)	0.0043 (5)	-0.0016 (4)	0.0008 (4)
C4	0.0144 (6)	0.0155 (6)	0.0098 (5)	0.0044 (5)	-0.0002 (4)	0.0005 (4)
C5	0.0161 (6)	0.0153 (6)	0.0137 (5)	0.0018 (5)	0.0018 (4)	0.0028 (4)
C6	0.0202 (6)	0.0120 (6)	0.0158 (6)	0.0039 (5)	0.0004 (5)	0.0004 (4)
C7	0.0153 (6)	0.0139 (6)	0.0108 (5)	0.0045 (5)	-0.0005 (4)	0.0000 (4)
C8	0.0173 (6)	0.0153 (6)	0.0122 (5)	0.0052 (5)	-0.0006 (4)	0.0008 (4)
C9	0.0134 (6)	0.0130 (6)	0.0101 (5)	0.0033 (5)	-0.0015 (4)	0.0005 (4)
C10	0.0313 (8)	0.0248 (7)	0.0201 (6)	0.0023 (7)	0.0041 (6)	0.0003 (5)
C11	0.0319 (8)	0.0319 (8)	0.0293 (7)	0.0117 (7)	0.0000 (6)	0.0078 (6)

Geometric parameters (Å, °)

O1—C1	1.2535 (16)	C4—C9	1.4119 (18)
O2—C1	1.2529 (17)	C5—C6	1.4061 (17)
O3—C3	1.2156 (15)	C5—H3	0.954 (18)
O4—C8	1.2195 (16)	C6—C7	1.3775 (19)
N1—C8 ⁱ	1.3909 (17)	C6—H4	0.963 (16)
N1—C3	1.3963 (17)	C7—C9 ⁱ	1.4135 (18)
N1—C2	1.4669 (15)	C7—C8	1.4834 (16)
N2—C10	1.4771 (18)	C8—N1 ⁱ	1.3909 (17)
N2—C11	1.4811 (19)	C9—C9 ⁱ	1.412 (2)
N2—H5	1.006 (19)	C9—C7 ⁱ	1.4135 (18)
N2—H6	0.94 (2)	C10—H7	0.958 (19)
C1—C2	1.5410 (18)	C10—H8	0.999 (18)
C2—H1	0.924 (18)	C10—H9	0.97 (2)
C2—H2	0.961 (16)	C11—H12	0.977 (19)
C3—C4	1.4872 (16)	C11—H11	0.98 (2)
C4—C5	1.3804 (19)	C11—H10	0.98 (2)

C8 ⁱ —N1—C3	125.18 (10)	C6—C5—H3	119.6 (9)
C8 ⁱ —N1—C2	116.13 (10)	C7—C6—C5	120.39 (12)
C3—N1—C2	118.08 (10)	C7—C6—H4	121.9 (9)
C10—N2—C11	112.51 (11)	C5—C6—H4	117.7 (9)
C10—N2—H5	108.9 (11)	C6—C7—C9 ⁱ	120.41 (11)
C11—N2—H5	109.7 (10)	C6—C7—C8	120.22 (11)
C10—N2—H6	109.1 (13)	C9 ⁱ —C7—C8	119.36 (11)
C11—N2—H6	110.9 (12)	O4—C8—N1 ⁱ	120.54 (11)
H5—N2—H6	105.5 (16)	O4—C8—C7	121.96 (12)
O2—C1—O1	126.66 (12)	N1 ⁱ —C8—C7	117.50 (11)
O2—C1—C2	117.51 (11)	C4—C9—C9 ⁱ	119.72 (14)
O1—C1—C2	115.81 (11)	C4—C9—C7 ⁱ	121.20 (11)
N1—C2—C1	111.40 (10)	C9 ⁱ —C9—C7 ⁱ	119.08 (14)
N1—C2—H1	106.2 (10)	N2—C10—H7	107.9 (11)
C1—C2—H1	110.7 (11)	N2—C10—H8	110.6 (10)
N1—C2—H2	107.6 (10)	H7—C10—H8	111.8 (14)
C1—C2—H2	112.6 (10)	N2—C10—H9	105.1 (11)
H1—C2—H2	108.1 (14)	H7—C10—H9	110.1 (15)
O3—C3—N1	121.18 (11)	H8—C10—H9	111.0 (14)
O3—C3—C4	122.08 (11)	N2—C11—H12	110.3 (11)
N1—C3—C4	116.74 (11)	N2—C11—H11	106.1 (12)
C5—C4—C9	120.10 (11)	H12—C11—H11	110.3 (15)
C5—C4—C3	119.99 (11)	N2—C11—H10	110.0 (11)
C9—C4—C3	119.92 (11)	H12—C11—H10	109.6 (15)
C4—C5—C6	120.29 (12)	H11—C11—H10	110.4 (16)
C4—C5—H3	120.1 (9)		
C8 ⁱ —N1—C2—C1	79.11 (13)	C3—C4—C5—C6	-179.17 (10)
C3—N1—C2—C1	-92.46 (13)	C4—C5—C6—C7	0.01 (19)
O2—C1—C2—N1	23.91 (16)	C5—C6—C7—C9 ⁱ	-0.44 (19)
O1—C1—C2—N1	-157.63 (11)	C5—C6—C7—C8	178.71 (10)
C8 ⁱ —N1—C3—O3	-178.82 (10)	C6—C7—C8—O4	-2.53 (19)
C2—N1—C3—O3	-8.08 (17)	C9 ⁱ —C7—C8—O4	176.63 (11)
C8 ⁱ —N1—C3—C4	1.85 (17)	C6—C7—C8—N1 ⁱ	177.33 (10)
C2—N1—C3—C4	172.59 (9)	C9 ⁱ —C7—C8—N1 ⁱ	-3.50 (17)
O3—C3—C4—C5	0.90 (18)	C5—C4—C9—C9 ⁱ	-0.3 (2)
N1—C3—C4—C5	-179.78 (10)	C3—C4—C9—C9 ⁱ	179.21 (12)
O3—C3—C4—C9	-178.65 (10)	C5—C4—C9—C7 ⁱ	179.58 (10)
N1—C3—C4—C9	0.67 (17)	C3—C4—C9—C7 ⁱ	-0.87 (18)
C9—C4—C5—C6	0.38 (19)		

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

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

<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>
N2—H5 \cdots O2	1.006 (19)	1.76 (2)	2.7358 (18)	163.5 (16)

supporting information

N2—H6···O1 ⁱⁱ	0.94 (2)	2.13 (2)	2.8419 (18)	131.8 (17)
N2—H6···O1 ⁱⁱⁱ	0.94 (2)	2.13 (2)	2.935 (2)	142.9 (17)

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