IUCrData

ISSN 2414-3146

Diethyl 2,2′-bipyridine-4,4′-dicarboxylate

D. Paul Rillema,[a]* Curtis Moore[b] and Venugopal KomReddy[a]

[a]Department of Chemistry, Wichita State University, Wichita, KS 67260, USA, and [b]Crystallographic laboratory, University of California, San Diego, LaJolla, CA 92093, USA. *Correspondence e-mail: paul.rillema@wichita.edu

Received 20 September 2016
Accepted 3 October 2016

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

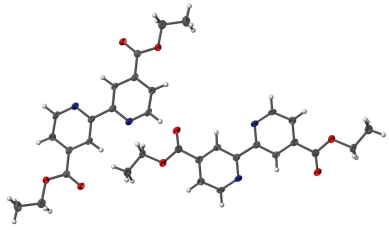
Keywords: crystal structure; bipyridine; dicarboxylate; hydrogen bonding; bidentate ligand; electron-withdrawing group.

CCDC reference: 1507876

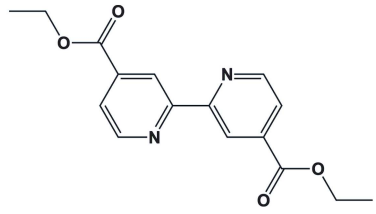
Structural data: full structural data are available from iucrdata.iucr.org

The title bipyridine derivative, $C_{16}H_{16}N_2O_4$, crystallized with two half molecules in the asymmetric unit. The whole molecules (*A* and *B*) are generated by inversion symmetry with the mid-points of the bridging C—C bonds of the bipyridine units being located on crystallographic inversion centers. In the crystal, molecules are linked by C—H···O hydrogen bonds, forming sheets parallel to (120). The sheets are linked by C—H···N hydrogen bonds, forming a three-dimensional framework.

3D view



Chemical scheme



Structure description

Dimmine ligands, such as the title compound, have been used to coordinate to transition metals, *viz*. Ru^{2+}, Pt^{2+}, and Re^{1+}, for use in solar energy conversion studies due to their excellent electronic properties (Cruz *et al.*, 2010; Rillema *et al.*, 2015; Villegas *et al.*, 2005). Upon photoexcitation, electrons are channeled from the metal center to the diimmine ligand on its pathway to the ground state.

The molecular structure of the two independent molecules of the title compound (*A* and *B*) are illustrated in Fig. 1. In both molecules, the two pyridine rings are arranged such that the pyridine N atoms are *trans* to one another. Molecule *A* is more planar than molecule *B*, with the ethyl carboxylate group [C—C—O—C(═O)] being inclined to the pyridine ring by 2.11 (15)° in *A*, and 5.69 (15)° in *B*.

The bond lengths and bond angles of the title free ligand are basically the same as those observed for the coordinated ligand in Pt(bph)(4,4′-diethoxycarbonyl-2,2′-bipyridine) (Rillema *et al.*, 2015). Upon coordination to transition metals, the two pyridine rings have the pyridine N atoms *cis* to one another, resulting in π–π delocalization over the whole ligand.

In the crystal, molecules are linked by C—H···O hydrogen bonds (Table 1), forming sheets parallel to (120), as illustrated in Fig. 2. The sheets are linked by C—H···N hydrogen bonds, forming a three-dimensional framework (Table 1 and Fig. 3).

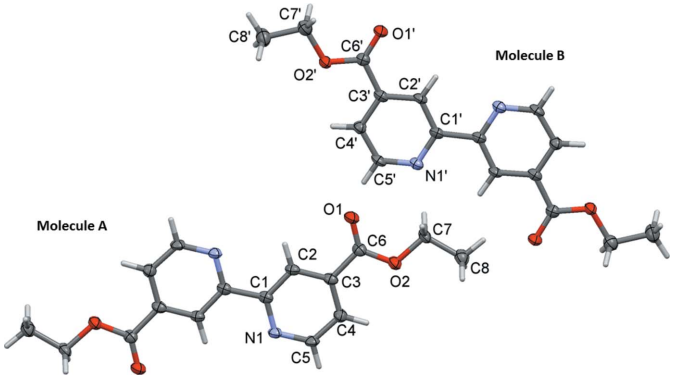


Figure 1
The molecular structure of the two independent molecules (*A* and *B*) of the title compound, showing the atom labeling [the unlabeled atoms are related to the labeled atoms by the symmetry code $(-x+1, -y, -z)$ for molecule *A*, and $(-x+1, -y+1, -z+1)$ for molecule *B*]. Displacement ellipsoids are drawn at the 50% probability level.

Synthesis and crystallization

The title compound was prepared in two steps according to previously published procedures. In step one, 4,4′-dimethyl-2,2′-bipyridine, purchased commercially, was oxidized forming 4,4′-dicarboxy-2,2′-bipyridine (Oki *et al.*, 1995). In step two, the dicarboxy compound was converted to the diethoxycarbonyl derivative (Ciana *et al.*, 1990). The vapor diffusion technique was used to obtain single crystals of the title compound. It was dissolved in dichloromethane and placed in a center vial, while the outer vial contained methanol.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

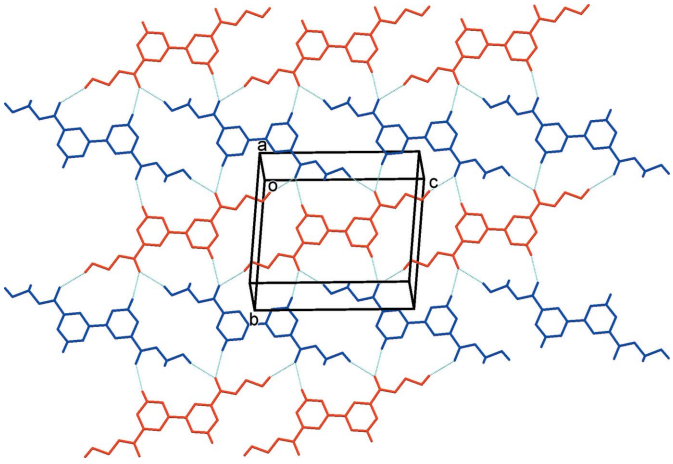


Figure 2
A view normal to plane (120) of the crystal packing of the title compound (molecule *A* is blue and molecule *B* is red). The hydrogen bonds are shown as dashed lines (see Table 1), and, for clarity, only the H atoms involved in hydrogen bonding have been included.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O1′^{i}	0.95	2.49	3.421 (3)	167
C8—H8B···O1′^{ii}	0.98	2.52	3.465 (3)	161
C5′—H5′···O1^{iii}	0.95	2.47	3.404 (3)	167
C8′—H8′A···O1^{iv}	0.98	2.58	3.518 (3)	161
C7—H7B···N1′	0.99	2.58	3.565 (4)	172

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{16}N_2O_4$
M_r	300.31
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	3.9059 (8), 13.493 (3), 13.767 (3)
α, β, γ (°)	92.212 (7), 93.163 (7), 93.016 (7)
V (Å^3)	722.8 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.13 × 0.08 × 0.06
Data collection	
Diffractometer	Bruker APEXII Ultra
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.066, 0.092
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10150, 2664, 1699
R_{int}	0.054
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.603
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.141, 1.02
No. of reflections	2664
No. of parameters	201
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.59, −0.26

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), SHEXLS2014 (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008).

Acknowledgements

We are grateful for support from the National Science Foundation (EPSCOR), the Wichita State University Office of Research, and the Department of Energy.

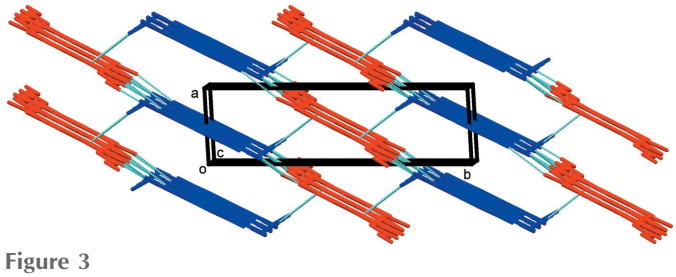


Figure 3
A view along the *c* axis of the crystal packing of the title compound (molecule *A* is blue and molecule *B* is red). The hydrogen bonds are shown as dashed lines (see Table 1), and, for clarity, only the H atoms involved in hydrogen bonding have been included.

References

Bruker (2013). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Ciana, L. D., Dressick, W. J. & Von Zelewsky, A. (1990). *J. Heterocycl. Chem.* **27**, 163–165.

Cruz, A. J., Kirgan, R., Siam, K., Heiland, P. & Rillema, D. P. (2010). *Inorg. Chim. Acta*, **363**, 2496–2505.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Oki, A. R. & Morgan, R. J. (1995). *Synth. Commun.* **25**, 4093–4097.

Rillema, D. P., Stoyanov, S., Cruz, A., Nguyen, H., Moore, C., Huang, W., Siam, K., Jehan, A. & KomReddy, V. (2015). *Dalton Trans.* **44**, 17075–17090.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Villegas, J. M., Stoyanov, S. R., Reibenspies, J. H. & Rillema, D. P. (2005). *Organometallics*, **24**, 395–404.

full crystallographic data

IUCrData (2016). **1**, x161547 [https://doi.org/10.1107/S2414314616015479]

Diethyl 2,2′-bipyridine-4,4′-dicarboxylate

D. Paul Rillema, Curtis Moore and Venugopal KomReddy

Diethyl 2,2′-bipyridine-4,4′-dicarboxylate

Crystal data

$C_{16}H_{16}N_2O_4$
M_r = 300.31
Triclinic, $P\overline{1}$
a = 3.9059 (8) Å
b = 13.493 (3) Å
c = 13.767 (3) Å
α = 92.212 (7)°
β = 93.163 (7)°
γ = 93.016 (7)°
V = 722.8 (3) Å^3
Z = 2
$F(000)$ = 316
D_x = 1.380 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2248 reflections
θ = 3.0–25.0°
μ = 0.10 mm^{-1}
T = 100 K
Plate, colorless
0.13 × 0.08 × 0.06 mm

Data collection

Bruker APEXII Ultra diffractometer
Radiation source: Micro Focus Rotating Anode, Bruker TXS
Double Bounce Multilayer Mirrors monochromator
Detector resolution: 7.9 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2013)
T_{min} = 0.066, T_{max} = 0.092
10150 measured reflections
2664 independent reflections
1699 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 25.4°, θ_{min} = 1.5°
h = −4→4
k = −16→16
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.141
S = 1.02
2664 reflections
201 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
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2 + 0.352P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.6443 (6)	−0.08269 (16)	0.09213 (16)	0.0229 (6)
O1	0.1227 (5)	0.21648 (14)	0.24091 (14)	0.0322 (5)
O2	0.2666 (5)	0.12418 (13)	0.36775 (13)	0.0267 (5)
C1	0.5052 (6)	−0.00246 (18)	0.05424 (19)	0.0213 (6)
C2	0.3798 (7)	0.0728 (2)	0.1117 (2)	0.0227 (6)
H2	0.2878	0.1291	0.0827	0.027*
C3	0.3909 (7)	0.06454 (19)	0.2116 (2)	0.0230 (7)
C4	0.5353 (7)	−0.0181 (2)	0.2512 (2)	0.0250 (7)
H4	0.5496	−0.0255	0.3196	0.030*
C5	0.6573 (7)	−0.0889 (2)	0.1889 (2)	0.0243 (7)
H5	0.7558	−0.1452	0.2163	0.029*
C6	0.2460 (7)	0.1439 (2)	0.2732 (2)	0.0238 (7)
C7	0.1308 (7)	0.1979 (2)	0.43362 (19)	0.0268 (7)
H7A	−0.1157	0.2057	0.4167	0.032*
H7B	0.2562	0.2631	0.4290	0.032*
C8	0.1788 (8)	0.1608 (2)	0.5350 (2)	0.0322 (8)
H8A	0.0535	0.0963	0.5385	0.048*
H8B	0.0904	0.2084	0.5817	0.048*
H8C	0.4237	0.1535	0.5508	0.048*
N1′	0.6531 (6)	0.41872 (16)	0.40638 (16)	0.0225 (6)
O1′	0.1233 (5)	0.71739 (14)	0.26347 (13)	0.0307 (5)
O2′	0.2484 (5)	0.62205 (13)	0.13410 (13)	0.0257 (5)
C1′	0.5100 (6)	0.49830 (18)	0.44587 (19)	0.0210 (6)
C2′	0.3829 (7)	0.57364 (19)	0.39046 (19)	0.0214 (6)
H2′	0.2889	0.6296	0.4209	0.026*
C3′	0.3960 (7)	0.56565 (19)	0.2899 (2)	0.0213 (6)
C4′	0.5453 (7)	0.4843 (2)	0.2487 (2)	0.0231 (7)
H4′	0.5623	0.4774	0.1803	0.028*
C5′	0.6691 (7)	0.4135 (2)	0.3096 (2)	0.0241 (7)
H5′	0.7713	0.3580	0.2810	0.029*
C6′	0.2446 (7)	0.6440 (2)	0.2295 (2)	0.0219 (6)
C7′	0.0956 (8)	0.6935 (2)	0.0684 (2)	0.0325 (7)
H7′A	0.2167	0.7597	0.0789	0.039*
H7′B	−0.1497	0.6999	0.0808	0.039*
C8′	0.1316 (9)	0.6543 (2)	−0.0342 (2)	0.0401 (8)
H8′A	0.0362	0.7007	−0.0802	0.060*
H8′B	0.0070	0.5894	−0.0441	0.060*
H8′C	0.3750	0.6473	−0.0452	0.060*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0252 (13)	0.0172 (12)	0.0269 (14)	0.0071 (10)	0.0006 (10)	0.0006 (10)
O1	0.0430 (13)	0.0242 (11)	0.0301 (12)	0.0145 (10)	−0.0005 (10)	−0.0027 (9)
O2	0.0306 (11)	0.0268 (11)	0.0235 (11)	0.0094 (9)	0.0026 (8)	−0.0026 (8)
C1	0.0165 (14)	0.0190 (15)	0.0278 (15)	0.0007 (12)	−0.0008 (12)	−0.0017 (12)
C2	0.0215 (15)	0.0172 (14)	0.0293 (17)	0.0037 (12)	−0.0014 (12)	0.0005 (12)
C3	0.0185 (15)	0.0202 (15)	0.0301 (17)	0.0034 (12)	−0.0001 (12)	−0.0015 (12)
C4	0.0248 (16)	0.0262 (16)	0.0246 (16)	0.0055 (13)	0.0021 (13)	0.0008 (13)
C5	0.0242 (15)	0.0193 (15)	0.0305 (17)	0.0093 (12)	0.0016 (12)	0.0038 (12)
C6	0.0201 (15)	0.0250 (16)	0.0258 (17)	0.0035 (13)	−0.0015 (12)	−0.0023 (13)
C7	0.0290 (16)	0.0262 (15)	0.0255 (16)	0.0089 (13)	0.0022 (12)	−0.0072 (12)
C8	0.0318 (18)	0.0359 (18)	0.0294 (18)	0.0072 (14)	0.0050 (13)	−0.0032 (14)
N1′	0.0224 (13)	0.0187 (12)	0.0264 (14)	0.0045 (10)	0.0011 (10)	−0.0022 (10)
O1′	0.0428 (13)	0.0249 (11)	0.0259 (12)	0.0169 (10)	0.0033 (9)	−0.0007 (9)
O2′	0.0327 (11)	0.0242 (11)	0.0206 (11)	0.0105 (9)	−0.0005 (8)	−0.0023 (8)
C1′	0.0195 (15)	0.0157 (15)	0.0278 (15)	0.0015 (12)	0.0021 (12)	−0.0021 (12)
C2′	0.0220 (15)	0.0157 (14)	0.0269 (17)	0.0057 (12)	0.0047 (12)	−0.0030 (12)
C3′	0.0176 (14)	0.0177 (14)	0.0282 (17)	0.0015 (12)	0.0024 (12)	−0.0046 (12)
C4′	0.0235 (15)	0.0240 (15)	0.0221 (15)	0.0053 (13)	0.0010 (12)	−0.0006 (13)
C5′	0.0228 (15)	0.0184 (14)	0.0312 (18)	0.0066 (12)	0.0033 (12)	−0.0067 (12)
C6′	0.0194 (15)	0.0208 (15)	0.0252 (17)	0.0008 (12)	0.0003 (12)	−0.0004 (12)
C7′	0.0352 (18)	0.0308 (17)	0.0319 (18)	0.0045 (14)	0.0061 (14)	−0.0019 (14)
C8′	0.044 (2)	0.047 (2)	0.0287 (19)	0.0099 (16)	0.0006 (15)	−0.0062 (15)

Geometric parameters (Å, º)

N1—C1	1.347 (3)	N1′—C1′	1.346 (3)
N1—C5	1.336 (3)	N1′—C5′	1.336 (3)
O1—C6	1.203 (3)	O1′—C6′	1.209 (3)
O2—C6	1.338 (3)	O2′—C6′	1.336 (3)
O2—C7	1.460 (3)	O2′—C7′	1.474 (3)
C1—C1^{i}	1.496 (5)	C1′—C1′^{ii}	1.496 (5)
C1—C2	1.389 (4)	C1′—C2′	1.390 (4)
C2—H2	0.9500	C2′—H2′	0.9500
C2—C3	1.382 (4)	C2′—C3′	1.388 (4)
C3—C4	1.392 (4)	C3′—C4′	1.386 (4)
C3—C6	1.494 (4)	C3′—C6′	1.496 (4)
C4—H4	0.9500	C4′—H4′	0.9500
C4—C5	1.381 (4)	C4′—C5′	1.384 (4)
C5—H5	0.9500	C5′—H5′	0.9500
C7—H7A	0.9900	C7′—H7′A	0.9900
C7—H7B	0.9900	C7′—H7′B	0.9900
C7—C8	1.507 (4)	C7′—C8′	1.505 (4)
C8—H8A	0.9800	C8′—H8′A	0.9800
C8—H8B	0.9800	C8′—H8′B	0.9800
C8—H8C	0.9800	C8′—H8′C	0.9800

C5—N1—C1	117.6 (2)	C5′—N1′—C1′	117.3 (2)
C6—O2—C7	115.9 (2)	C6′—O2′—C7′	116.5 (2)
N1—C1—C1^{i}	116.4 (3)	N1′—C1′—C1′^{ii}	116.4 (3)
N1—C1—C2	122.5 (2)	N1′—C1′—C2′	122.8 (2)
C2—C1—C1^{i}	121.1 (3)	C2′—C1′—C1′^{ii}	120.8 (3)
C1—C2—H2	120.4	C1′—C2′—H2′	120.6
C3—C2—C1	119.1 (2)	C3′—C2′—C1′	118.8 (2)
C3—C2—H2	120.4	C3′—C2′—H2′	120.6
C2—C3—C4	118.6 (2)	C2′—C3′—C6′	119.1 (2)
C2—C3—C6	119.1 (2)	C4′—C3′—C2′	118.7 (2)
C4—C3—C6	122.3 (3)	C4′—C3′—C6′	122.1 (2)
C3—C4—H4	120.7	C3′—C4′—H4′	120.8
C5—C4—C3	118.5 (3)	C5′—C4′—C3′	118.5 (3)
C5—C4—H4	120.7	C5′—C4′—H4′	120.8
N1—C5—C4	123.5 (2)	N1′—C5′—C4′	123.8 (3)
N1—C5—H5	118.2	N1′—C5′—H5′	118.1
C4—C5—H5	118.2	C4′—C5′—H5′	118.1
O1—C6—O2	124.3 (3)	O1′—C6′—O2′	123.9 (2)
O1—C6—C3	123.6 (3)	O1′—C6′—C3′	123.6 (2)
O2—C6—C3	112.1 (2)	O2′—C6′—C3′	112.4 (2)
O2—C7—H7A	110.3	O2′—C7′—H7′A	110.3
O2—C7—H7B	110.3	O2′—C7′—H7′B	110.3
O2—C7—C8	106.9 (2)	O2′—C7′—C8′	107.2 (2)
H7A—C7—H7B	108.6	H7′A—C7′—H7′B	108.5
C8—C7—H7A	110.3	C8′—C7′—H7′A	110.3
C8—C7—H7B	110.3	C8′—C7′—H7′B	110.3
C7—C8—H8A	109.5	C7′—C8′—H8′A	109.5
C7—C8—H8B	109.5	C7′—C8′—H8′B	109.5
C7—C8—H8C	109.5	C7′—C8′—H8′C	109.5
H8A—C8—H8B	109.5	H8′A—C8′—H8′B	109.5
H8A—C8—H8C	109.5	H8′A—C8′—H8′C	109.5
H8B—C8—H8C	109.5	H8′B—C8′—H8′C	109.5

Symmetry codes: (i) −*x*+1, −*y*, −*z*; (ii) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O1′^{iii}	0.95	2.49	3.421 (3)	167
C8—H8*B*···O1′^{iv}	0.98	2.52	3.465 (3)	161
C5′—H5′···O1^{v}	0.95	2.47	3.404 (3)	167
C8′—H8′*A*···O1^{vi}	0.98	2.58	3.518 (3)	161
C7—H7*B*···N1′	0.99	2.58	3.565 (4)	172

Symmetry codes: (iii) *x*+1, *y*−1, *z*; (iv) −*x*, −*y*+1, −*z*+1; (v) *x*+1, *y*, *z*; (vi) −*x*, −*y*+1, −*z*.