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Structural, Hirshfeld surface and three-dimensional interaction-energy studies of 1,3,5-triethyl 2-amino-3,5-dicyano-4,6-bis(4-fluorophenyl)cyclohex-1-ene-1,3,5-tricarboxylate

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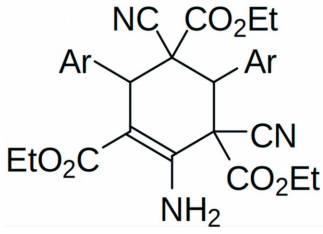
In the title compound, $C_{29}H_{27}F_2N_3O_6$, which crystallizes in the monoclinic space group $P2_1/c$, the cyclohexenone ring is puckered and adopts an envelope conformation. The crystal structure features various intermolecular interactions, such as N—H···O, C—H···N and C—H···O. These interactions were investigated using Hirshfeld surface analysis and the three-dimensional interaction energies were calculated using the B3LYP/6–31 G(d,p) energy density model.

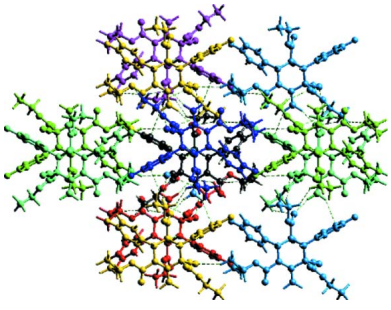
1. Chemical context

Organic compounds containing hetero atoms such as fluorine, nitrogen, sulfur and oxygen exhibit significant biological activities such as antioxidant (Fu *et al.*, 2010), insecticidal (Carbonnelle *et al.*, 2005), antibacterial, antifungal (Sener *et al.*, 2000), anti-inflammatory (Khanum *et al.*, 2004), anti-convulsant, analgesic and antitumor (Kushwaha *et al.*, 2011). These compounds find a wide range of applications in the fields of agriculture and biochemistry as well as in the pharmaceuticals industry. Hence, hetero organic compounds have attracted the attention of chemists with the aim of designing and synthesizing new organic compounds. The title compound was synthesized, its structure was studied by X-ray diffraction techniques and a computational analysis was performed to understand the intermolecular interactions.



2. Structural commentary

In the title compound (Fig. 1), the cyclohexenone ring (C1–C6) is puckered [maximum puckering amplitude Q = 0.554 (4) (3) Å and exhibits an envelope conformation on atom C2 (Cremer & Pople, 1975). The bond lengths and bond angles agree with those of previously reported related



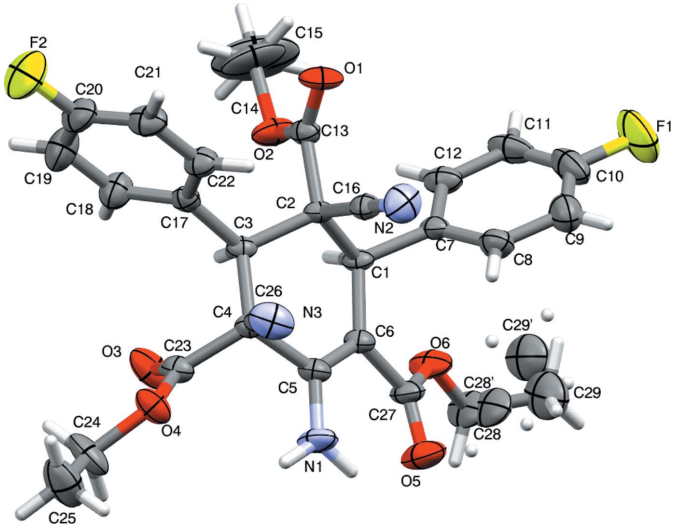


Figure 1
View of the title molecule with displacement ellipsoids drawn at 40% probability level.

compounds (Gunasekaran *et al.*, 2009; Mertsalov *et al.*, 2021; Chandana *et al.*, 2021; Ganesha, Sreenatha *et al.*, 2023; Ganesha, Nizamuddin *et al.*, 2023; Ganesha *et al.*, 2022; Sreenatha *et al.*, 2018, 2020, 2022; Lakshminarayana *et al.*, 2009, 2010, 2022; Madan Kumar *et al.*, 2018; HariPrasada *et al.*, 2023). The dihedral angle between the mean plane of the cyclohexenone (C1–C6) and fluorobenzene rings (C7–C12 and C17–C22) are 62.3 (2) and 84.9 (2)°, respectively, confirming the non-planarity of the molecule and also the equatorial orientation of the rings. The carboxylate group at the C2 position is oriented *+syn-clinical*, *--anti-clinical*, *+anti-clinical* and *–syn-clinical* to the mean plane of the C1–C6 ring with torsion angles C1—C2—C13—O2 = 50.3 (4)°, C1—C2—C13—O1 = −131.3 (4)°, C3—C2—C13—O1 = 110.6 (4)° and C3—C2—C13—O2 = −67.8 (4)°. The orientation of other two carboxylate groups at the C4 and C5 positions are described by the torsion angles C1—C6—C27—O6 = −15.4 (5)° (*–syn-periplanar*), C1—C6—C27—O5 = 167.2 (4)° (*+anti-periplanar*), C5—C6—C27—O5 = −17.2 (6)° (*–anti-periplanar*), C5—C6—C27—O6 = 160.1 (3)° (*+anti-periplanar*) and C3—C4—C23—O3 = 44.9 (5)° (*+syn-clinal*), C3—C4—C23—O4 = −136.4 (3)° (*–anti-clinal*), C5—C4—C23—O3 = −75.8 (4)° (*–syn-clinal*), C5—C4—C23—O4 = 102.9 (3)° (*+anti-clinal*). The orientation is due to the intermolecular N—H···O and C—H···O interactions.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14*B*···N3^{i}	0.97	2.60	3.420 (7)	143
C24—H24*B*···O3^{ii}	0.97	2.58	3.483 (6)	156
N1—H1*N*···O5	0.87 (2)	2.03 (4)	2.662 (5)	128 (4)
N1—H2*N*···O1^{iii}	0.88 (2)	2.25 (3)	3.064 (4)	155 (4)
N1—H2*N*···O4	0.88 (2)	2.61 (4)	3.152 (5)	121 (4)

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

3. Supramolecular features

In the crystal, the molecules are held together by an intermolecular interactions of the types N1—H2*N*···O1, C14—H14*B*···N3, and C24—H24*B*···O3 (Table 1), enclosing an $R_2^2(10)$ closed ring motif, propagating along the [101] direction (Figs. 2 and 3).

4. Database survey

A survey of the Cambridge Structural Database (CSD version 5.41, update of November 2022; Groom *et al.*, 2016) reveals one nearly comparable derivative, triethyl 2-(5-nitro-2*H*-indazol-2-yl)propane-1,2,3-tricarboxylate (NUPQAS; Boul-

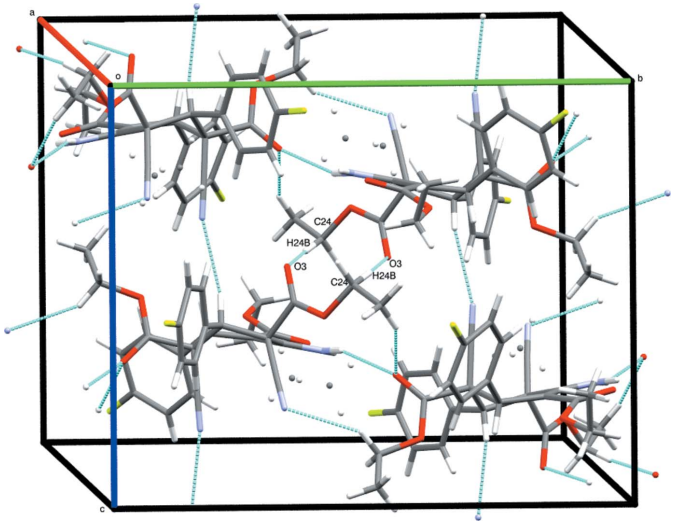


Figure 2
Packing of the molecules along the *b* axis, showing the $R_2^2(10)$ ring motif.

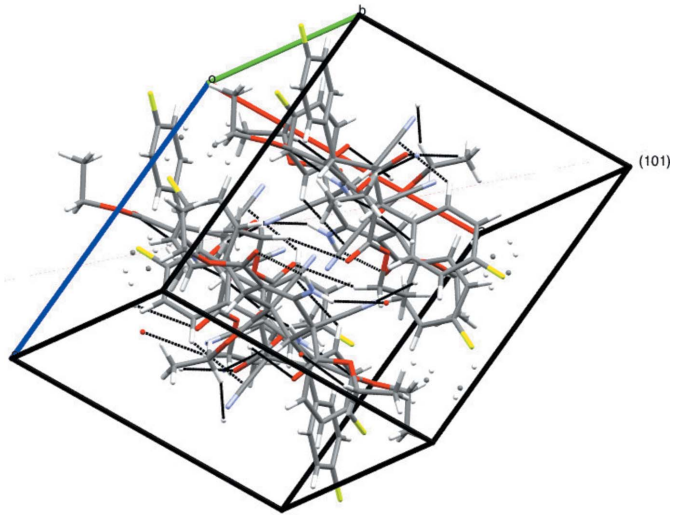


Figure 3
The intermolecular interactions enclosing the $R_2^2(10)$ ring motif propagating along the [101] direction.

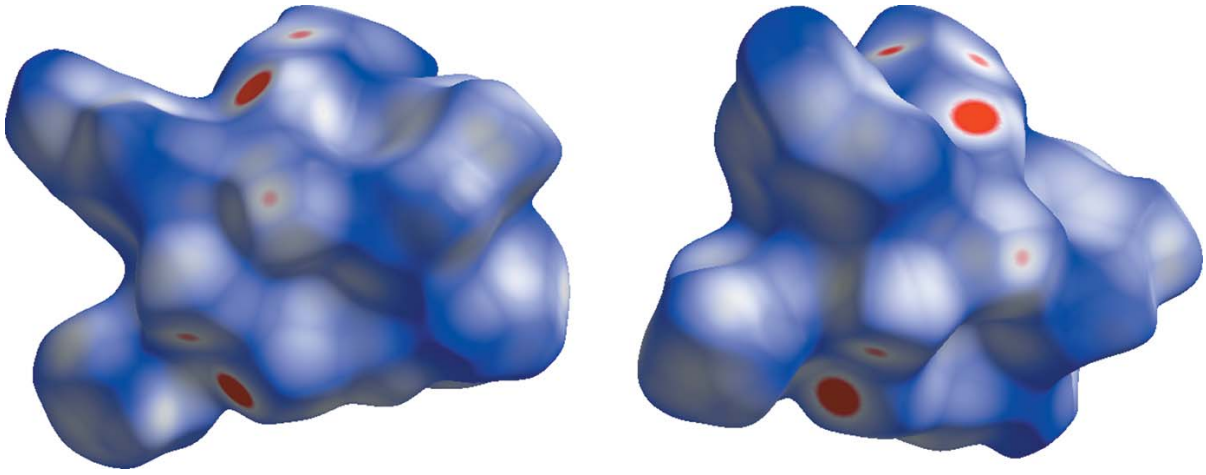


Figure 4
Hirshfeld surface mapped over d_{norm} (front and back views are shown).

haoua *et al.*, 2015) in which intermolecular C—H···O and C—H···N bonds are observed.

5. Hirshfeld surfaces and 2D fingerprint calculations

The Hirshfeld surface (HS) mapped over d_{norm} was generated using *CrystalExplorer17.5* (Spackman *et al.*, 2009) with a colour scale of −0.3124 a.u. for red to +1.7877 a.u. for blue. The area and volume of the d_{norm} surface are 681.46 Å^2 and 527.71 Å^3, respectively. The front and rear views of the Hirshfeld surface mapped over d_{norm} are depicted in Fig. 4. The bright-red circular spots on d_{norm} indicates the presence of intermolecular N1—H2*N*···O1, C14—H14*B*···N3 and C24—H24*B*···O3 interactions. The percentage contribution from different intermolecular interactions towards the formation of a three dimensional Hirshfeld surface (HS) was computed using two-dimensional fingerprint calculations (Fig. 5). The results showed that the H···H (40.1%) contacts make the major contribution to the crystal packing, while the C···H (11.2%), N···H (14.7%), H···F (16.3%), H···O (14.5%) contacts also make a significant contribution to the total area of the HS surface.

6. Three-dimensional-framework analysis of interaction energies

CrystalExplorer 17.5 software calculates interaction energies between crystal molecular pairs. Energy calculations were carried out using the B3LYP/6-31G(d,p) basis set within a default radius of 3.8 Å (Turner *et al.*, 2015, 2017; Gavezzotti,

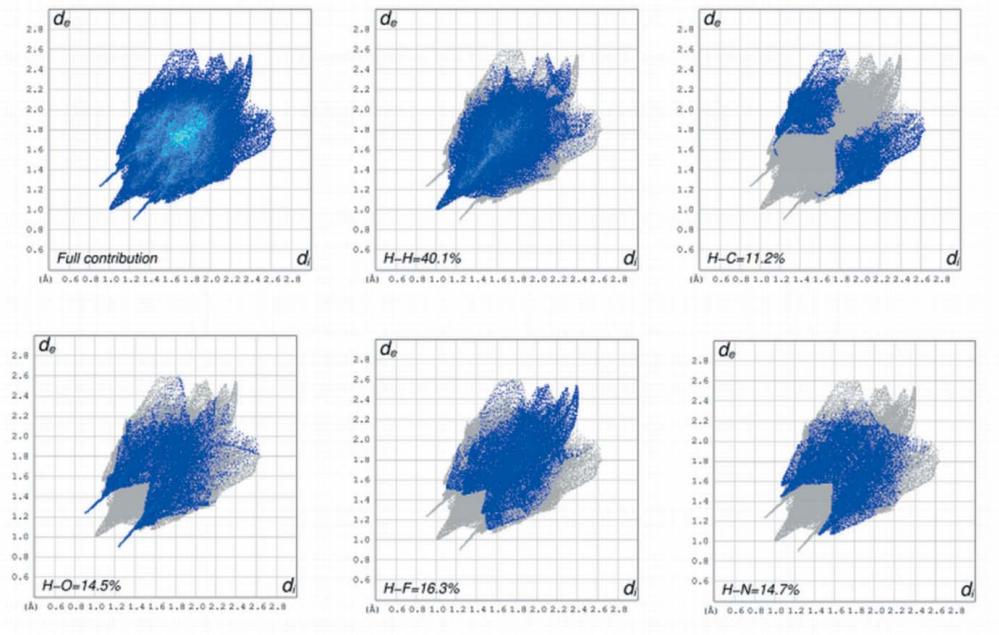
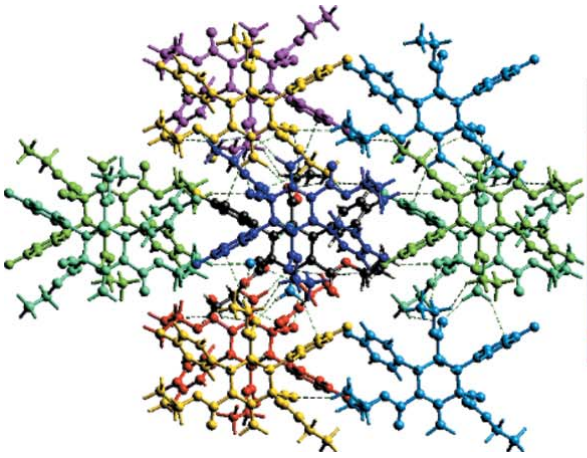


Figure 5
Two-dimensional fingerprint plots showing the pecentage contributions of various interatomic contacts.



Color Code	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	9.26	B3LYP/6-31G(d,p)	-24.5	-5.1	-66.3	40.9	-62.1
	2	-x, y+1/2, -z+1/2	9.29	B3LYP/6-31G(d,p)	-38.9	-10.0	-48.4	37.7	-67.4
	2	x, -y+1/2, z+1/2	12.86	B3LYP/6-31G(d,p)	-1.2	-1.8	-25.5	11.5	-17.6
	2	x, y, z	12.09	B3LYP/6-31G(d,p)	-7.5	-4.7	-42.5	30.4	-29.6
	2	-x, y+1/2, -z+1/2	12.26	B3LYP/6-31G(d,p)	-4.6	-1.8	-20.2	9.2	-18.1
	2	x, -y+1/2, z+1/2	6.91	B3LYP/6-31G(d,p)	-9.2	-10.2	-60.9	32.5	-50.1
	1	-x, -y, -z	11.27	B3LYP/6-31G(d,p)	-5.9	-2.7	-25.5	18.4	-19.1

Figure 6
Visualization of the interaction energy values between the reference molecule and the constituents of a cluster within the default radius of 3.8 Å. The table gives information on the number of molecules (*N*) interacting with the reference nolecule in a cluster, the rotational symmetry (*Symop*) and the corresponding molecular centroid–centroid distances (*R*, in Å) and the interaction energies in component form.

2002; Grimme, 2006). The interaction of different molecules with the reference molecule (black ball-and-stick model at the centre) in the cluster of energy frameworks is depicted in Fig. 6. Fig. 7 depicts the energy frameworks, visualizing the strength of the interactions, with the Coulombic, dispersion and total energies shown in red, green and blue, respectively. The radii of the cylinders connecting the centroids of the molecules indicate the relative strengths of the interaction energies. A table of interaction energies in component form is given in the table in Fig. 6. The highest total interaction energy (E_{tot} = −67.4 kJ mol^{-1}) is associated with a pair of yellow molecules with the short centroid distance R = 9.29 Å with rotational symmetry $-x, y+\frac{1}{2}, -z+\frac{1}{2}$, while the lowest total interaction energy (E_{tot} = −17.6 kJ mol^{-1}) was observed for a pair of green molecules interacting at the longer centroid distance R = 12.86 Å; this is in accordance with the classical laws of electrostatics. In each of the energy terms, the dispersion component is dominant over the others.

7. Synthesis and crystallization

Piperidine (6 mmol) was added to ethyl cyanoacetate (30 mmol) and the mixture was stirred for 10 min. Then 4-fluorobenzaldehyde (20 mmol) was added dropwise and during the addition, the temperature of the reaction mass rose to 333 K (it should not be cooled), and the mass was stirred for 30 min. The temperature slowly came down to 293–298 K over 30 min. The progress of the reaction was monitored by TLC and found to be complete. Methylene chloride (30 ml) and water (20 ml) were added and the mixture was stirred for 10 min. The organic layer was separated and washed with sat. aq. NaCl solution and dried over anhydrous Na_2SO_4, then concentrated under reduced pressure to get the crude product. This was purified by silica gel column chromatography using *n*-heptane/ethyl acetate as eluent. The mixture was quenched in cold water and the organic layer was extracted with ethyl acetate, washed with 5% sodium bicarbonate solution, and dried over anhydrous sodium sulfate. Slow evaporation of the solvent lead to crystals of the title compound, which were recrystallized from ethanol solution.

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were placed at idealized positions and allowed to ride on their parent atoms with C—H

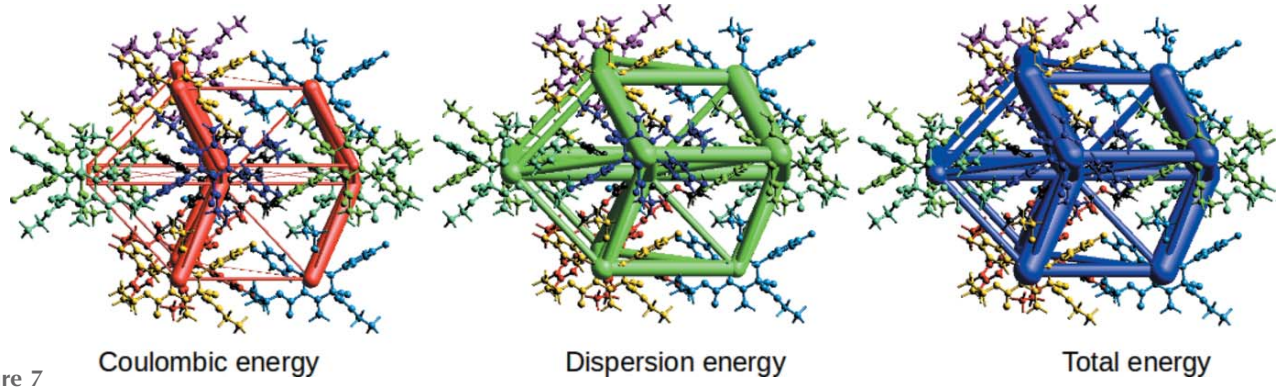


Figure 7
Three-dimensional energy frameworks of Coulombic, dispersion and total energy terms.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{29}H_{27}F_2N_3O_6$
M_r	551.53
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	297
a, b, c (Å)	12.0884 (11), 17.0492 (16), 13.5966 (11)
β (°)	100.008 (3)
V (Å^3)	2759.6 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.14 × 0.09 × 0.04
Data collection	
Diffractometer	Bruker Kappa APEXIII PHOTON II
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	52965, 4869, 3477
R_{int}	0.141
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.087, 0.214, 1.14
No. of reflections	4869
No. of parameters	386
No. of restraints	47
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.31

Computer programs: *APEX3* and *SAINT* (Bruker, 2014), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *PLATON* (Spek, 2020).

distances in the range 0.93–0.98 Å and U_{iso}(H) = 1.2U_{eq}(C) (1.5 for methyl H atoms).

Acknowledgements

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supporting information

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Structural, Hirshfeld surface and three-dimensional interaction-energy studies of 1,3,5-triethyl 2-amino-3,5-dicyano-4,6-bis(4-fluorophenyl)cyclohex-1-ene-1,3,5-tricarboxylate

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Computing details

Data collection: *APEX3* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *SHELXL2018/3* (Sheldrick, 2015b); software used to prepare material for publication: *PLATON* (Spek, 2020).

1,3,5-Triethyl 2-amino-3,5-dicyano-4,6-bis(4-fluorophenyl)cyclohex-1-ene-1,3,5-tricarboxylate

Crystal data

$C_{29}H_{27}F_2N_3O_6$
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a = 12.0884 (11) Å
b = 17.0492 (16) Å
c = 13.5966 (11) Å
β = 100.008 (3)°
V = 2759.6 (4) Å^3
Z = 4
$F(000)$ = 1152
D_x = 1.328 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3477 reflections
θ = 2.9–25.1°
μ = 0.10 mm^{-1}
T = 297 K
Block, colorless
0.14 × 0.09 × 0.04 mm

Data collection

Bruker Kappa APEXIII PHOTON II diffractometer
Radiation source: fine focus sealed tube
φ and ω scans
52965 measured reflections
4869 independent reflections
3477 reflections with $I > 2\sigma(I)$
R_{int} = 0.141
θ_{max} = 25.0°, θ_{min} = 2.9°
h = −14→14
k = −20→20
l = −16→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.087
$wR(F^2)$ = 0.214
S = 1.14
4869 reflections
386 parameters
47 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.095P)^2 + 2.1236P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 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}	Occ. (<1)
C1	0.7198 (3)	0.2207 (2)	0.2001 (3)	0.0240 (8)	
H1	0.727769	0.231041	0.130783	0.029*	
C2	0.6104 (3)	0.2626 (2)	0.2181 (2)	0.0235 (8)	
C3	0.5101 (3)	0.2230 (2)	0.1488 (2)	0.0234 (8)	
H3	0.532115	0.221020	0.082740	0.028*	
C4	0.4967 (3)	0.1361 (2)	0.1785 (3)	0.0253 (8)	
C5	0.6106 (3)	0.0939 (2)	0.2085 (3)	0.0285 (8)	
C6	0.7102 (3)	0.1323 (2)	0.2112 (3)	0.0264 (8)	
C7	0.8219 (3)	0.2567 (2)	0.2671 (3)	0.0286 (8)	
C8	0.8565 (3)	0.2338 (2)	0.3650 (3)	0.0403 (10)	
H8	0.817146	0.194409	0.391282	0.048*	
C9	0.9480 (4)	0.2679 (3)	0.4252 (4)	0.0531 (12)	
H9	0.970380	0.252113	0.491150	0.064*	
C10	1.0048 (4)	0.3258 (3)	0.3841 (4)	0.0601 (14)	
C11	0.9741 (4)	0.3508 (3)	0.2875 (4)	0.0521 (13)	
H11	1.013665	0.390343	0.261732	0.062*	
C12	0.8822 (3)	0.3153 (2)	0.2293 (3)	0.0378 (10)	
H12	0.860441	0.331096	0.163341	0.045*	
C13	0.6100 (3)	0.3501 (2)	0.1913 (3)	0.0290 (8)	
C14	0.6296 (6)	0.4404 (3)	0.0641 (5)	0.085 (2)	
H14A	0.553966	0.451275	0.029724	0.102*	
H14B	0.646142	0.476250	0.120125	0.102*	
C15	0.7038 (9)	0.4537 (4)	−0.0001 (7)	0.143 (4)	
H15A	0.697339	0.507096	−0.022647	0.215*	
H15B	0.779025	0.444078	0.033956	0.215*	
H15C	0.686851	0.419104	−0.056445	0.215*	
C16	0.6009 (3)	0.2580 (2)	0.3251 (3)	0.0282 (8)	
C17	0.3999 (3)	0.2679 (2)	0.1335 (3)	0.0255 (8)	
C18	0.3455 (3)	0.2816 (3)	0.0369 (3)	0.0428 (11)	
H18	0.378204	0.264155	−0.016208	0.051*	
C19	0.2441 (4)	0.3203 (3)	0.0172 (4)	0.0556 (13)	
H19	0.208054	0.328936	−0.048125	0.067*	
C20	0.1976 (3)	0.3458 (3)	0.0969 (4)	0.0489 (12)	
C21	0.2487 (3)	0.3355 (2)	0.1932 (4)	0.0430 (11)	
H21	0.215853	0.354255	0.245598	0.052*	
C22	0.3500 (3)	0.2967 (2)	0.2117 (3)	0.0352 (9)	
H22	0.385888	0.289508	0.277302	0.042*	
C23	0.4342 (3)	0.0933 (2)	0.0843 (3)	0.0303 (9)	
C24	0.2967 (4)	−0.0024 (3)	0.0223 (4)	0.0538 (13)	

H24A	0.268639	0.030494	−0.034869	0.065*	
H24B	0.348193	−0.040468	0.002475	0.065*	
C25	0.2039 (5)	−0.0422 (4)	0.0563 (4)	0.0697 (16)	
H25A	0.164771	−0.074136	0.003303	0.105*	
H25B	0.232526	−0.074708	0.112636	0.105*	
H25C	0.153279	−0.004020	0.075435	0.105*	
C26	0.4322 (3)	0.1278 (2)	0.2620 (3)	0.0312 (9)	
C27	0.8120 (3)	0.0845 (2)	0.2178 (3)	0.0356 (9)	
C28	0.998 (3)	0.084 (2)	0.1734 (17)	0.058 (5)	0.345 (12)
H28A	1.029815	0.108563	0.120192	0.070*	0.345 (12)
H28B	0.984697	0.029090	0.158581	0.070*	0.345 (12)
C29	1.0710 (15)	0.0958 (13)	0.2720 (15)	0.084 (5)	0.345 (12)
H29A	1.142674	0.071719	0.271532	0.126*	0.345 (12)
H29B	1.081077	0.150867	0.285153	0.126*	0.345 (12)
H29C	1.036386	0.072146	0.323178	0.126*	0.345 (12)
C28′	1.0074 (13)	0.0836 (10)	0.2141 (11)	0.063 (3)	0.655 (12)
H28C	1.016442	0.061117	0.280600	0.076*	0.655 (12)
H28D	1.013141	0.041797	0.166848	0.076*	0.655 (12)
C29′	1.0950 (6)	0.1438 (6)	0.2095 (8)	0.070 (3)	0.655 (12)
H29D	1.167949	0.120150	0.225539	0.105*	0.655 (12)
H29E	1.085169	0.165536	0.143452	0.105*	0.655 (12)
H29F	1.088455	0.184765	0.256673	0.105*	0.655 (12)
F1	1.0955 (3)	0.3596 (2)	0.4425 (3)	0.0998 (13)	
F2	0.0967 (2)	0.3833 (2)	0.0775 (3)	0.0818 (10)	
N1	0.5985 (3)	0.01657 (19)	0.2255 (3)	0.0421 (9)	
H1N	0.658 (3)	−0.013 (2)	0.240 (3)	0.050*	
H2N	0.536 (2)	−0.010 (2)	0.215 (3)	0.050*	
N2	0.5956 (3)	0.2536 (2)	0.4077 (3)	0.0475 (10)	
N3	0.3848 (3)	0.1197 (2)	0.3262 (3)	0.0478 (10)	
O1	0.5874 (3)	0.40133 (16)	0.2450 (2)	0.0477 (8)	
O2	0.6346 (3)	0.36003 (16)	0.1017 (2)	0.0444 (8)	
O3	0.4589 (3)	0.10243 (19)	0.0037 (2)	0.0515 (9)	
O4	0.3547 (2)	0.04598 (17)	0.10520 (19)	0.0394 (7)	
O5	0.8213 (3)	0.01601 (17)	0.2428 (3)	0.0567 (9)	
O6	0.8963 (2)	0.12367 (16)	0.1887 (2)	0.0464 (8)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0252 (19)	0.0198 (18)	0.0296 (19)	0.0023 (15)	0.0116 (15)	−0.0003 (15)
C2	0.0297 (19)	0.0174 (17)	0.0250 (18)	0.0007 (15)	0.0095 (15)	0.0000 (14)
C3	0.0286 (19)	0.0199 (18)	0.0238 (18)	0.0012 (15)	0.0109 (15)	−0.0016 (14)
C4	0.0258 (19)	0.0227 (19)	0.0297 (19)	0.0009 (15)	0.0112 (15)	0.0006 (15)
C5	0.035 (2)	0.0190 (18)	0.033 (2)	−0.0016 (16)	0.0098 (16)	−0.0033 (15)
C6	0.031 (2)	0.0200 (18)	0.0295 (19)	0.0007 (16)	0.0084 (15)	−0.0031 (15)
C7	0.0266 (19)	0.0179 (18)	0.042 (2)	0.0016 (15)	0.0066 (16)	−0.0019 (16)
C8	0.038 (2)	0.028 (2)	0.054 (3)	−0.0041 (18)	0.006 (2)	−0.0009 (19)
C9	0.043 (3)	0.055 (3)	0.057 (3)	0.001 (2)	−0.005 (2)	−0.010 (2)

C10	0.035 (3)	0.054 (3)	0.089 (4)	−0.007 (2)	0.003 (3)	−0.030 (3)
C11	0.035 (2)	0.031 (2)	0.094 (4)	−0.012 (2)	0.023 (3)	−0.015 (2)
C12	0.031 (2)	0.028 (2)	0.057 (3)	0.0002 (18)	0.0158 (19)	0.0007 (19)
C13	0.0242 (19)	0.0237 (19)	0.040 (2)	−0.0014 (16)	0.0065 (16)	−0.0012 (17)
C14	0.125 (5)	0.039 (3)	0.102 (5)	0.024 (3)	0.049 (4)	0.042 (3)
C15	0.218 (10)	0.061 (4)	0.180 (8)	0.010 (5)	0.113 (8)	0.055 (5)
C16	0.027 (2)	0.025 (2)	0.033 (2)	0.0031 (15)	0.0077 (16)	−0.0020 (16)
C17	0.0251 (19)	0.0210 (18)	0.031 (2)	−0.0038 (15)	0.0060 (15)	0.0016 (15)
C18	0.040 (2)	0.050 (3)	0.038 (2)	0.009 (2)	0.0066 (19)	0.002 (2)
C19	0.046 (3)	0.070 (3)	0.047 (3)	0.014 (3)	−0.002 (2)	0.011 (2)
C20	0.025 (2)	0.042 (3)	0.078 (4)	0.0076 (19)	0.001 (2)	0.004 (2)
C21	0.030 (2)	0.036 (2)	0.065 (3)	0.0027 (19)	0.016 (2)	−0.007 (2)
C22	0.031 (2)	0.034 (2)	0.042 (2)	0.0045 (18)	0.0097 (18)	−0.0013 (18)
C23	0.029 (2)	0.025 (2)	0.038 (2)	−0.0019 (16)	0.0098 (17)	−0.0040 (16)
C24	0.048 (3)	0.061 (3)	0.054 (3)	−0.024 (2)	0.013 (2)	−0.032 (2)
C25	0.064 (3)	0.075 (4)	0.068 (3)	−0.037 (3)	0.005 (3)	−0.005 (3)
C26	0.034 (2)	0.0210 (19)	0.040 (2)	−0.0043 (16)	0.0117 (18)	−0.0006 (16)
C27	0.036 (2)	0.019 (2)	0.052 (3)	0.0042 (17)	0.0066 (19)	−0.0006 (18)
C28	0.021 (6)	0.054 (6)	0.100 (12)	0.014 (5)	0.010 (9)	−0.010 (10)
C29	0.043 (8)	0.086 (10)	0.118 (11)	−0.001 (8)	0.000 (8)	−0.017 (9)
C28′	0.027 (5)	0.057 (4)	0.105 (10)	0.012 (4)	0.008 (7)	−0.008 (8)
C29′	0.031 (4)	0.075 (6)	0.105 (7)	−0.002 (4)	0.011 (4)	−0.003 (5)
F1	0.058 (2)	0.097 (3)	0.131 (3)	−0.0340 (19)	−0.0192 (19)	−0.035 (2)
F2	0.0386 (16)	0.087 (2)	0.115 (3)	0.0305 (16)	0.0012 (16)	−0.003 (2)
N1	0.036 (2)	0.0187 (18)	0.072 (3)	−0.0024 (15)	0.0125 (19)	0.0036 (17)
N2	0.056 (2)	0.055 (2)	0.034 (2)	0.0074 (19)	0.0148 (17)	0.0013 (17)
N3	0.060 (2)	0.046 (2)	0.045 (2)	−0.0092 (19)	0.030 (2)	−0.0024 (17)
O1	0.064 (2)	0.0228 (15)	0.059 (2)	0.0075 (14)	0.0186 (16)	−0.0112 (14)
O2	0.064 (2)	0.0279 (15)	0.0453 (17)	0.0084 (14)	0.0213 (15)	0.0111 (13)
O3	0.063 (2)	0.059 (2)	0.0383 (17)	−0.0270 (17)	0.0225 (15)	−0.0144 (15)
O4	0.0377 (16)	0.0429 (16)	0.0396 (16)	−0.0169 (13)	0.0127 (12)	−0.0084 (13)
O5	0.0423 (18)	0.0280 (17)	0.100 (3)	0.0084 (14)	0.0130 (17)	0.0077 (16)
O6	0.0277 (15)	0.0306 (15)	0.085 (2)	0.0050 (12)	0.0201 (15)	−0.0051 (15)

Geometric parameters (Å, º)

C1—C6	1.520 (5)	C17—C22	1.399 (5)
C1—C7	1.530 (5)	C18—C19	1.377 (6)
C1—C2	1.559 (5)	C18—H18	0.9300
C1—H1	0.9800	C19—C20	1.375 (7)
C2—C16	1.480 (5)	C19—H19	0.9300
C2—C13	1.535 (5)	C20—C21	1.359 (6)
C2—C3	1.555 (5)	C20—F2	1.362 (5)
C3—C17	1.520 (5)	C21—C22	1.375 (6)
C3—C4	1.551 (5)	C21—H21	0.9300
C3—H3	0.9800	C22—H22	0.9300
C4—C26	1.491 (5)	C23—O3	1.194 (4)
C4—C5	1.545 (5)	C23—O4	1.322 (4)

C4—C23	1.552 (5)	C24—C25	1.453 (6)
C5—N1	1.351 (5)	C24—O4	1.472 (5)
C5—C6	1.365 (5)	C24—H24A	0.9700
C6—C27	1.466 (5)	C24—H24B	0.9700
C7—C8	1.380 (6)	C25—H25A	0.9600
C7—C12	1.387 (5)	C25—H25B	0.9600
C8—C9	1.385 (6)	C25—H25C	0.9600
C8—H8	0.9300	C26—N3	1.133 (5)
C9—C10	1.376 (7)	C27—O5	1.216 (5)
C9—H9	0.9300	C27—O6	1.334 (5)
C10—F1	1.365 (5)	C28—O6	1.45 (3)
C10—C11	1.369 (7)	C28—C29	1.484 (18)
C11—C12	1.386 (6)	C28—H28A	0.9700
C11—H11	0.9300	C28—H28B	0.9700
C12—H12	0.9300	C29—H29A	0.9600
C13—O1	1.200 (4)	C29—H29B	0.9600
C13—O2	1.314 (4)	C29—H29C	0.9600
C14—C15	1.375 (8)	C28′—C29′	1.484 (14)
C14—O2	1.460 (5)	C28′—O6	1.494 (18)
C14—H14A	0.9700	C28′—H28C	0.9700
C14—H14B	0.9700	C28′—H28D	0.9700
C15—H15A	0.9600	C29′—H29D	0.9600
C15—H15B	0.9600	C29′—H29E	0.9600
C15—H15C	0.9600	C29′—H29F	0.9600
C16—N2	1.139 (5)	N1—H1N	0.874 (19)
C17—C18	1.383 (5)	N1—H2N	0.875 (19)

C6—C1—C7	113.9 (3)	C22—C17—C3	123.8 (3)
C6—C1—C2	110.9 (3)	C19—C18—C17	121.7 (4)
C7—C1—C2	109.9 (3)	C19—C18—H18	119.1
C6—C1—H1	107.2	C17—C18—H18	119.1
C7—C1—H1	107.2	C20—C19—C18	118.0 (4)
C2—C1—H1	107.2	C20—C19—H19	121.0
C16—C2—C13	106.7 (3)	C18—C19—H19	121.0
C16—C2—C3	112.8 (3)	C21—C20—F2	119.2 (4)
C13—C2—C3	107.9 (3)	C21—C20—C19	122.6 (4)
C16—C2—C1	110.1 (3)	F2—C20—C19	118.1 (4)
C13—C2—C1	112.1 (3)	C20—C21—C22	118.6 (4)
C3—C2—C1	107.4 (3)	C20—C21—H21	120.7
C17—C3—C4	112.8 (3)	C22—C21—H21	120.7
C17—C3—C2	115.9 (3)	C21—C22—C17	121.2 (4)
C4—C3—C2	111.2 (3)	C21—C22—H22	119.4
C17—C3—H3	105.3	C17—C22—H22	119.4
C4—C3—H3	105.3	O3—C23—O4	125.7 (4)
C2—C3—H3	105.3	O3—C23—C4	122.1 (3)
C26—C4—C5	108.3 (3)	O4—C23—C4	112.1 (3)
C26—C4—C3	112.4 (3)	C25—C24—O4	108.0 (4)
C5—C4—C3	112.6 (3)	C25—C24—H24A	110.1

C26—C4—C23	109.9 (3)	O4—C24—H24A	110.1
C5—C4—C23	106.4 (3)	C25—C24—H24B	110.1
C3—C4—C23	107.0 (3)	O4—C24—H24B	110.1
N1—C5—C6	125.8 (4)	H24A—C24—H24B	108.4
N1—C5—C4	112.4 (3)	C24—C25—H25A	109.5
C6—C5—C4	121.7 (3)	C24—C25—H25B	109.5
C5—C6—C27	117.6 (3)	H25A—C25—H25B	109.5
C5—C6—C1	123.7 (3)	C24—C25—H25C	109.5
C27—C6—C1	118.6 (3)	H25A—C25—H25C	109.5
C8—C7—C12	118.0 (4)	H25B—C25—H25C	109.5
C8—C7—C1	122.6 (3)	N3—C26—C4	178.2 (4)
C12—C7—C1	119.3 (4)	O5—C27—O6	121.7 (4)
C7—C8—C9	121.9 (4)	O5—C27—C6	125.9 (4)
C7—C8—H8	119.0	O6—C27—C6	112.4 (3)
C9—C8—H8	119.0	O6—C28—C29	101.3 (19)
C10—C9—C8	117.7 (5)	O6—C28—H28A	111.5
C10—C9—H9	121.2	C29—C28—H28A	111.5
C8—C9—H9	121.2	O6—C28—H28B	111.5
F1—C10—C11	118.9 (5)	C29—C28—H28B	111.5
F1—C10—C9	118.3 (5)	H28A—C28—H28B	109.3
C11—C10—C9	122.8 (4)	C28—C29—H29A	109.5
C10—C11—C12	117.9 (4)	C28—C29—H29B	109.5
C10—C11—H11	121.0	H29A—C29—H29B	109.5
C12—C11—H11	121.0	C28—C29—H29C	109.5
C11—C12—C7	121.6 (4)	H29A—C29—H29C	109.5
C11—C12—H12	119.2	H29B—C29—H29C	109.5
C7—C12—H12	119.2	C29′—C28′—O6	107.0 (12)
O1—C13—O2	125.6 (4)	C29′—C28′—H28C	110.3
O1—C13—C2	123.7 (3)	O6—C28′—H28C	110.3
O2—C13—C2	110.7 (3)	C29′—C28′—H28D	110.3
C15—C14—O2	112.7 (5)	O6—C28′—H28D	110.3
C15—C14—H14A	109.1	H28C—C28′—H28D	108.6
O2—C14—H14A	109.1	C28′—C29′—H29D	109.5
C15—C14—H14B	109.1	C28′—C29′—H29E	109.5
O2—C14—H14B	109.1	H29D—C29′—H29E	109.5
H14A—C14—H14B	107.8	C28′—C29′—H29F	109.5
C14—C15—H15A	109.5	H29D—C29′—H29F	109.5
C14—C15—H15B	109.5	H29E—C29′—H29F	109.5
H15A—C15—H15B	109.5	C5—N1—H1N	120 (3)
C14—C15—H15C	109.5	C5—N1—H2N	127 (3)
H15A—C15—H15C	109.5	H1N—N1—H2N	113 (4)
H15B—C15—H15C	109.5	C13—O2—C14	116.3 (4)
N2—C16—C2	178.5 (4)	C23—O4—C24	116.4 (3)
C18—C17—C22	117.8 (3)	C27—O6—C28	121.5 (14)
C18—C17—C3	118.4 (3)	C27—O6—C28′	113.9 (6)
C6—C1—C2—C16	70.5 (4)	C8—C7—C12—C11	−0.5 (6)
C7—C1—C2—C16	−56.4 (4)	C1—C7—C12—C11	178.8 (3)

C6—C1—C2—C13	−171.0 (3)	C16—C2—C13—O1	−10.8 (5)
C7—C1—C2—C13	62.1 (4)	C3—C2—C13—O1	110.6 (4)
C6—C1—C2—C3	−52.6 (4)	C1—C2—C13—O1	−131.3 (4)
C7—C1—C2—C3	−179.6 (3)	C16—C2—C13—O2	170.8 (3)
C16—C2—C3—C17	74.3 (4)	C3—C2—C13—O2	−67.8 (4)
C13—C2—C3—C17	−43.3 (4)	C1—C2—C13—O2	50.3 (4)
C1—C2—C3—C17	−164.3 (3)	C4—C3—C17—C18	−102.1 (4)
C16—C2—C3—C4	−56.4 (4)	C2—C3—C17—C18	128.1 (4)
C13—C2—C3—C4	−173.9 (3)	C4—C3—C17—C22	78.1 (4)
C1—C2—C3—C4	65.1 (3)	C2—C3—C17—C22	−51.8 (5)
C17—C3—C4—C26	−49.1 (4)	C22—C17—C18—C19	−1.7 (6)
C2—C3—C4—C26	83.1 (4)	C3—C17—C18—C19	178.5 (4)
C17—C3—C4—C5	−171.8 (3)	C17—C18—C19—C20	0.3 (7)
C2—C3—C4—C5	−39.6 (4)	C18—C19—C20—C21	1.2 (7)
C17—C3—C4—C23	71.6 (3)	C18—C19—C20—F2	−179.2 (4)
C2—C3—C4—C23	−156.2 (3)	F2—C20—C21—C22	179.2 (4)
C26—C4—C5—N1	60.7 (4)	C19—C20—C21—C22	−1.2 (7)
C3—C4—C5—N1	−174.3 (3)	C20—C21—C22—C17	−0.3 (6)
C23—C4—C5—N1	−57.4 (4)	C18—C17—C22—C21	1.7 (6)
C26—C4—C5—C6	−122.6 (4)	C3—C17—C22—C21	−178.5 (4)
C3—C4—C5—C6	2.4 (5)	C26—C4—C23—O3	167.2 (4)
C23—C4—C5—C6	119.3 (4)	C5—C4—C23—O3	−75.7 (5)
N1—C5—C6—C27	10.0 (6)	C3—C4—C23—O3	44.9 (5)
C4—C5—C6—C27	−166.2 (3)	C26—C4—C23—O4	−14.0 (4)
N1—C5—C6—C1	−174.7 (4)	C5—C4—C23—O4	103.0 (3)
C4—C5—C6—C1	9.1 (5)	C3—C4—C23—O4	−136.4 (3)
C7—C1—C6—C5	142.1 (3)	C5—C6—C27—O5	−17.2 (6)
C2—C1—C6—C5	17.4 (5)	C1—C6—C27—O5	167.2 (4)
C7—C1—C6—C27	−42.7 (4)	C5—C6—C27—O6	160.1 (3)
C2—C1—C6—C27	−167.4 (3)	C1—C6—C27—O6	−15.4 (5)
C6—C1—C7—C8	−41.2 (5)	O1—C13—O2—C14	−2.4 (6)
C2—C1—C7—C8	84.0 (4)	C2—C13—O2—C14	176.0 (4)
C6—C1—C7—C12	139.5 (3)	C15—C14—O2—C13	150.1 (7)
C2—C1—C7—C12	−95.3 (4)	O3—C23—O4—C24	3.5 (6)
C12—C7—C8—C9	0.4 (6)	C4—C23—O4—C24	−175.1 (3)
C1—C7—C8—C9	−179.0 (4)	C25—C24—O4—C23	−172.8 (4)
C7—C8—C9—C10	−0.3 (7)	O5—C27—O6—C28	7.9 (11)
C8—C9—C10—F1	−179.7 (4)	C6—C27—O6—C28	−169.6 (10)
C8—C9—C10—C11	0.3 (7)	O5—C27—O6—C28′	−14.7 (9)
F1—C10—C11—C12	179.5 (4)	C6—C27—O6—C28′	167.8 (7)
C9—C10—C11—C12	−0.5 (7)	C29—C28—O6—C27	−94 (2)
C10—C11—C12—C7	0.6 (6)	C29′—C28′—O6—C27	−161.1 (8)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14*B*···N3^{i}	0.97	2.60	3.420 (7)	143
C24—H24*B*···O3^{ii}	0.97	2.58	3.483 (6)	156

N1—H1*N*···O5	0.87 (2)	2.03 (4)	2.662 (5)	128 (4)
N1—H2*N*···O1^{iii}	0.88 (2)	2.25 (3)	3.064 (4)	155 (4)
N1—H2*N*···O4	0.88 (2)	2.61 (4)	3.152 (5)	121 (4)

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*+1, −*y*, −*z*; (iii) −*x*+1, *y*−1/2, −*z*+1/2.