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Bis(*N*,*N*′-diphenylbenzamidinium) fumarate

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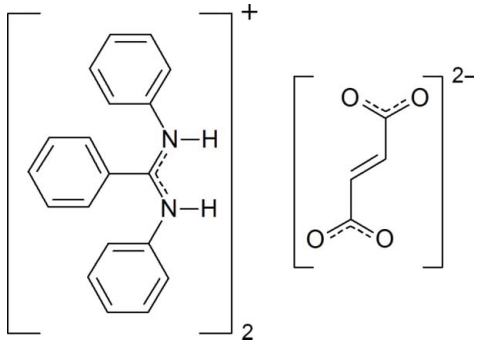
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.001 Å; R factor = 0.042; wR factor = 0.107; data-to-parameter ratio = 21.6.

The crystal structure of the title compound, $2C_{19}H_{17}N_2^+\cdot C_4H_2O_4^{2-}$, consists of centrosymmetric trimers built up of two crystallographically independent *N*,*N*′-diphenylbenzamidinium cations and one fumarate dianion, which is located on a centre of inversion. The components of the trimers are linked by N—H···O hydrogen bonding. In the cation, the outer rings make dihedral angles of 53.66 (5) and 78.38 (5)° with the central ring. The two outer rings make a dihdral angle of 81.49 (5)°.

Related literature

For the structure of *N*,*N*′-diphenylbenzamidine, see: Alcock *et al.* (1988) and for the structure of *N*,*N*′-diphenylbenzamidinium nitrate, see: Barker *et al.* (1999). For metal complexes of *N*,*N*′-diphenylbenzamidine, see: Davies *et al.* (2001); Jiang *et al.* (2005); Cotton *et al.* (1996, 1997).



Experimental

Crystal data

$2C_{19}H_{17}N_2^+\cdot C_4H_2O_4^{2-}$
M_r = 330.39
Monoclinic, $P2_1/n$
a = 10.5972 (3) Å
b = 8.8275 (3) Å
c = 18.7710 (7) Å
β = 102.346 (1)°
V = 1715.36 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 120 K
0.72 × 0.61 × 0.44 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2006)
T_{min} = 0.95, T_{max} = 0.96
41010 measured reflections
5009 independent reflections
4976 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.107
S = 1.00
4876 reflections
226 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N19—H4···O3	0.88	1.79	2.673 (1)	178
N12—H9···O4	0.90	1.74	2.634 (2)	172

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SMART* (Bruker, 2006); data reduction: *SMART*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2180).

References

Alcock, N. W., Barker, J. & Kilner, M. (1988). *Acta Cryst.* C**44**, 712–715.
Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–?.
Barker, J., Errington, W. & Wallbridge, M. G. H. (1999). *Acta Cryst.* C**55**, 1583–1585.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Bruker (2006). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cotton, F. A., Daniels, L. M., Falvello, L. R., Matonic, J. H. & Murillo, C. A. (1997). *Inorg. Chim. Acta*, **256**, 269–275.
Cotton, F. A., Daniels, L. M., Maloney, D. J. & Murillo, C. A. (1996). *Inorg. Chim. Acta*, **249**, 9–11.
Davies, R. P., Linton, D. J., Schooler, P., Snaith, R. & Wheatley, A. E. H. (2001). *Eur. J. Inorg. Chem.* pp. 619–622.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Jiang, X., Bollinger, J. C., Baik, M.-H. & Lee, D. (2005). *Chem. Commun.* pp. 1043–1045.

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Bis(*N*,*N*′-diphenylbenzamidinium) fumarate

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S1. Comment

N,*N*′-Diphenylbenzamidine is widely used as a ligand in metal complexes and can act as a bridging (Jiang *et al.*, 2005) or a bidentate (Davies *et al.*, 2001) ligand. An important feature of many complexes with bridging bonding mode is metal-metal bond formation in dinuclear compounds (Cotton *et al.*, 1997; Cotton *et al.*, 1996). The crystal structure of *N*,*N*′-diphenylbenzamidine (Alcock *et al.*, 1988) and its nitrate salt (Barker *et al.*, 1999) have been reported previously. As part of an investigation of cocrystal synthesis, the *N*,*N*′-diphenylbenzamidine fumarate salt was obtained and the crystal and molecular structure was determined to identify the product. The asymmetric unit consist of one *N*,*N*′-diphenylbenzamidinium cation and half a fumarate dianion, which is located on a centre of inversion (Fig. 1). In the title compound there is a small difference in conformation of amidinium cation compared to *N*,*N*′-diphenylbenzamidine nitrate. In the amidinium cation the plane of the central phenyl ring is twisted by 53.7° and 78.4° with respect to the plane of the terminal phenyl rings 1 and 2 (Fig. 1). These values are slightly different from that in *N*,*N*′-diphenylbenzamidine nitrate in which a dihedral angle of 65.8° is observed (Barker *et al.*, 1999). In the crystal structure of the title compound the amidinium cations are connected by the fumarate dianions via intermolecular N–H···O hydrogen bonds into trimers that are located on centres of inversion (Fig. 2 and Table 1).

S2. Experimental

The title compound was prepared by dissolving *N*,*N*′-diphenylbenzamidine (0.054 g, 0.2 mmol) and fumaric acid (0.012 g, 0.1 mmol) in 5 ml of hot ethanol. Slow evaporation of the solution resulted in the formation of colorless prisms.

S3. Refinement

All H atoms were located in a difference map, but were positioned with idealized geometry and refined with soft restraints on the bond lengths and angles to regularise their geometry (C—H in the range of 0.93–0.98 and N—H in the range of 0.86—0.89 Å) and with U_{iso}(H) in the range 1.2-1.5 times U_{eq} of the parent atom.

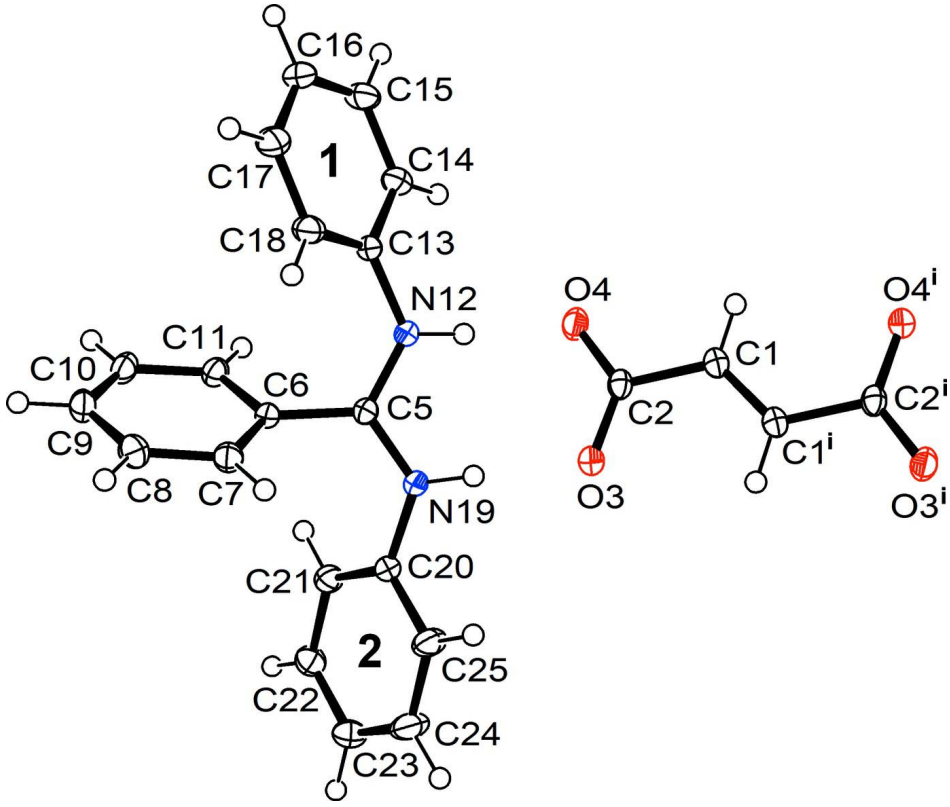

Figure 1

The molecular structure of the title compound with labelling and displacement ellipsoids at the 50% probability level (symmetry code for equivalent atoms: i = -x+2, -y, -z+2). 1 and 2 distinguish the two independent terminal rings.

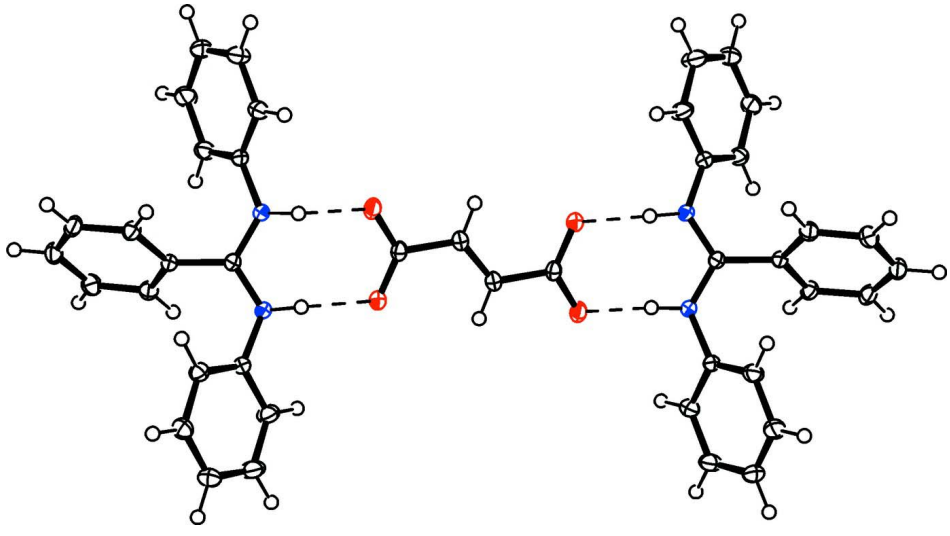

Figure 2

Crystal structure of the title compound with view of the trimers (hydrogen bonding is indicated by dashed lines).

Bis(*N*,*N*′-diphenylbenzamidinium) fumarate

Crystal data

$2C_{19}H_{17}N_2^+ \cdot C_4H_2O_4^{2-}$
$M_r = 330.39$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 10.5972$ (3) Å
$b = 8.8275$ (3) Å
$c = 18.7710$ (7) Å
$\beta = 102.346$ (1)°
$V = 1715.36$ (10) Å^3
$Z = 4$
$F(000) = 696.00$
$D_x = 1.279$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9851 reflections
$\theta = 3$–30°
$\mu = 0.08$ mm^{-1}
$T = 120$ K
Prism fragment, colorless
0.72 × 0.61 × 0.44 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*APEX2*; Bruker, 2006)
$T_{min} = 0.95$, $T_{max} = 0.96$
41010 measured reflections
5009 independent reflections
4876 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 30.0°$, $\theta_{min} = 2.0°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 26$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.107$
$S = 1.00$
4976 reflections
226 parameters
0 restraints
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + (0.06P)^2 + 0.63P]$ where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.94300 (8)	0.03374 (10)	0.99406 (5)	0.0188
C2	0.86998 (8)	0.07821 (10)	0.91958 (5)	0.0172
O3	0.91578 (6)	0.04194 (8)	0.86516 (3)	0.0213
O4	0.76557 (6)	0.14853 (8)	0.91690 (4)	0.0229
C5	0.63464 (8)	0.08298 (9)	0.73154 (4)	0.0158
C6	0.53733 (8)	0.06749 (10)	0.66218 (4)	0.0155
C7	0.53685 (9)	−0.06272 (10)	0.62033 (5)	0.0202
C8	0.43586 (9)	−0.08628 (12)	0.56046 (5)	0.0247
C9	0.33852 (9)	0.02100 (12)	0.54165 (5)	0.0239
C10	0.34143 (8)	0.15261 (11)	0.58227 (5)	0.0220
C11	0.44042 (8)	0.17580 (10)	0.64315 (5)	0.0189
N12	0.59750 (7)	0.09379 (9)	0.79444 (4)	0.0177
C13	0.47079 (8)	0.07070 (10)	0.80659 (4)	0.0171
C14	0.43162 (9)	0.16661 (11)	0.85652 (5)	0.0223
C15	0.30805 (10)	0.15224 (13)	0.87010 (5)	0.0268
C16	0.22460 (9)	0.04177 (14)	0.83488 (5)	0.0282

C17	0.26682 (10)	−0.05734 (13)	0.78741 (6)	0.0285
C18	0.39004 (9)	−0.04455 (11)	0.77341 (5)	0.0230
N19	0.76104 (7)	0.08174 (9)	0.73401 (4)	0.0182
C20	0.82262 (8)	0.11807 (10)	0.67587 (4)	0.0173
C21	0.77945 (8)	0.23541 (10)	0.62732 (5)	0.0200
C22	0.84978 (9)	0.27416 (11)	0.57528 (5)	0.0232
C23	0.96279 (10)	0.19753 (12)	0.57190 (5)	0.0259
C24	1.00596 (10)	0.08164 (13)	0.62091 (6)	0.0305
C25	0.93605 (9)	0.04137 (12)	0.67293 (6)	0.0260
H11	0.9043	0.0548	1.0339	0.0224*
H91	0.2695	0.0056	0.4998	0.0277*
H101	0.2769	0.2275	0.5692	0.0264*
H111	0.4430	0.2649	0.6712	0.0230*
H141	0.4887	0.2423	0.8804	0.0269*
H151	0.2816	0.2217	0.9032	0.0324*
H161	0.1385	0.0352	0.8434	0.0313*
H171	0.2125	−0.1372	0.7639	0.0336*
H211	0.7042	0.2873	0.6302	0.0239*
H221	0.8201	0.3536	0.5423	0.0286*
H231	1.0108	0.2256	0.5354	0.0309*
H241	1.0854	0.0287	0.6200	0.0370*
H251	0.9653	−0.0391	0.7075	0.0301*
H3	0.6030	−0.1359	0.6324	0.0240*
H4	0.8118	0.0660	0.7773	0.0225*
H8	0.4178	−0.1146	0.7427	0.0269*
H9	0.6581	0.1188	0.8341	0.0217*
H12	0.4343	−0.1762	0.5325	0.0293*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0190 (4)	0.0215 (4)	0.0147 (3)	−0.0001 (3)	0.0011 (3)	0.0002 (3)
C2	0.0163 (4)	0.0173 (4)	0.0164 (4)	0.0003 (3)	−0.0002 (3)	−0.0025 (3)
O3	0.0175 (3)	0.0294 (3)	0.0162 (3)	0.0017 (2)	0.0017 (2)	0.0008 (2)
O4	0.0186 (3)	0.0281 (3)	0.0196 (3)	−0.0029 (2)	−0.0010 (2)	0.0042 (2)
C5	0.0146 (3)	0.0169 (4)	0.0154 (3)	0.0006 (3)	0.0024 (3)	0.0014 (3)
C6	0.0138 (3)	0.0185 (4)	0.0141 (3)	0.0008 (3)	0.0026 (3)	0.0001 (3)
C7	0.0201 (4)	0.0209 (4)	0.0195 (4)	−0.0020 (3)	0.0037 (3)	0.0023 (3)
C8	0.0252 (4)	0.0269 (5)	0.0212 (4)	−0.0069 (3)	0.0035 (3)	−0.0027 (4)
C9	0.0197 (4)	0.0322 (5)	0.0180 (4)	0.0005 (3)	−0.0001 (3)	−0.0046 (3)
C10	0.0156 (4)	0.0261 (4)	0.0225 (4)	0.0048 (3)	0.0002 (3)	0.0010 (3)
C11	0.0166 (4)	0.0193 (4)	0.0200 (4)	0.0000 (3)	0.0021 (3)	0.0018 (3)
N12	0.0132 (3)	0.0248 (4)	0.0148 (3)	−0.0010 (3)	0.0024 (2)	0.0001 (3)
C13	0.0141 (3)	0.0228 (4)	0.0147 (3)	0.0021 (3)	0.0035 (3)	0.0011 (3)
C14	0.0222 (4)	0.0268 (4)	0.0192 (4)	−0.0026 (3)	0.0070 (3)	−0.0005 (3)
C15	0.0256 (5)	0.0334 (5)	0.0245 (4)	−0.0005 (4)	0.0125 (4)	0.0035 (4)
C16	0.0187 (4)	0.0434 (6)	0.0246 (4)	0.0046 (4)	0.0090 (3)	−0.0010 (4)
C17	0.0233 (4)	0.0391 (6)	0.0246 (4)	−0.0023 (4)	0.0083 (4)	−0.0108 (4)

C18	0.0223 (4)	0.0271 (4)	0.0212 (4)	−0.0030 (3)	0.0085 (3)	−0.0048 (3)
N19	0.0134 (3)	0.0260 (4)	0.0149 (3)	0.0024 (3)	0.0026 (2)	0.0023 (3)
C20	0.0147 (3)	0.0212 (4)	0.0161 (4)	−0.0003 (3)	0.0036 (3)	0.0000 (3)
C21	0.0189 (4)	0.0208 (4)	0.0207 (4)	0.0010 (3)	0.0049 (3)	0.0026 (3)
C22	0.0249 (4)	0.0241 (4)	0.0210 (4)	0.0036 (3)	0.0058 (3)	−0.0007 (3)
C23	0.0245 (4)	0.0315 (5)	0.0244 (4)	0.0019 (4)	0.0111 (3)	−0.0022 (4)
C24	0.0221 (4)	0.0375 (6)	0.0357 (5)	0.0076 (4)	0.0148 (4)	0.0074 (4)
C25	0.0196 (4)	0.0315 (5)	0.0288 (5)	0.0092 (4)	0.0093 (3)	0.0077 (4)

Geometric parameters (Å, º)

C1—C1^{i}	1.3223 (17)	C14—C15	1.3924 (13)
C1—C2	1.4982 (11)	C14—H141	0.947
C1—H11	0.944	C15—C16	1.3857 (15)
C2—O3	1.2625 (11)	C15—H151	0.957
C2—O4	1.2603 (11)	C16—C17	1.3892 (15)
C5—C6	1.4842 (11)	C16—H161	0.961
C5—N12	1.3255 (10)	C17—C18	1.3906 (13)
C5—N19	1.3304 (10)	C17—H171	0.956
C6—C7	1.3917 (12)	C18—H8	0.935
C6—C11	1.3926 (12)	N19—C20	1.4228 (11)
C7—C8	1.3919 (13)	N19—H4	0.884
C7—H3	0.944	C20—C21	1.3908 (12)
C8—C9	1.3892 (14)	C20—C25	1.3909 (12)
C8—H12	0.950	C21—C22	1.3922 (12)
C9—C10	1.3864 (14)	C21—H211	0.931
C9—H91	0.962	C22—C23	1.3886 (14)
C10—C11	1.3912 (12)	C22—H221	0.943
C10—H101	0.945	C23—C24	1.3864 (15)
C11—H111	0.944	C23—H231	0.969
N12—C13	1.4239 (10)	C24—C25	1.3922 (13)
N12—H9	0.901	C24—H241	0.966
C13—C14	1.3907 (12)	C25—H251	0.967
C13—C18	1.3882 (12)		

C1^{i}—C1—C2	123.12 (10)	C15—C14—H141	120.5
C1^{i}—C1—H11	119.4	C14—C15—C16	120.40 (9)
C2—C1—H11	117.5	C14—C15—H151	118.6
C1—C2—O3	118.51 (8)	C16—C15—H151	121.0
C1—C2—O4	116.12 (8)	C15—C16—C17	119.28 (9)
O3—C2—O4	125.36 (8)	C15—C16—H161	119.7
C6—C5—N12	120.33 (7)	C17—C16—H161	121.0
C6—C5—N19	122.37 (7)	C16—C17—C18	120.95 (9)
N12—C5—N19	117.26 (7)	C16—C17—H171	121.1
C5—C6—C7	119.29 (7)	C18—C17—H171	118.0
C5—C6—C11	119.85 (8)	C17—C18—C13	119.23 (9)
C7—C6—C11	120.58 (8)	C17—C18—H8	119.7
C6—C7—C8	119.25 (8)	C13—C18—H8	121.1

C6—C7—H3	121.1	C5—N19—C20	126.50 (7)
C8—C7—H3	119.7	C5—N19—H4	116.3
C7—C8—C9	120.28 (9)	C20—N19—H4	116.8
C7—C8—H12	119.4	N19—C20—C21	122.00 (8)
C9—C8—H12	120.4	N19—C20—C25	117.56 (8)
C8—C9—C10	120.23 (8)	C21—C20—C25	120.17 (8)
C8—C9—H91	120.3	C20—C21—C22	119.49 (8)
C10—C9—H91	119.4	C20—C21—H211	119.6
C9—C10—C11	119.95 (8)	C22—C21—H211	120.9
C9—C10—H101	120.9	C21—C22—C23	120.57 (9)
C11—C10—H101	119.1	C21—C22—H221	119.3
C6—C11—C10	119.66 (8)	C23—C22—H221	120.1
C6—C11—H111	119.9	C22—C23—C24	119.65 (9)
C10—C11—H111	120.5	C22—C23—H231	119.7
C5—N12—C13	127.02 (7)	C24—C23—H231	120.6
C5—N12—H9	117.3	C23—C24—C25	120.28 (9)
C13—N12—H9	115.7	C23—C24—H241	120.7
N12—C13—C14	116.64 (8)	C25—C24—H241	119.1
N12—C13—C18	123.03 (8)	C24—C25—C20	119.83 (9)
C14—C13—C18	120.29 (8)	C24—C25—H251	121.0
C13—C14—C15	119.73 (9)	C20—C25—H251	119.2
C13—C14—H141	119.8		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N19—H4···O3	0.88	1.79	2.673 (1)	178
N12—H9···O4	0.90	1.74	2.634 (2)	172