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4-Bromo-N 2,N 2,N 6,N 6-tetraethylpyridine-2,6-dicarboxamide

Daniel T. de Lill

Ana de Bettencourt-Dias

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4-Bromo-*N*²,*N*²,*N*⁶,*N*⁶-tetraethylpyridine-2,6-dicarboxamide

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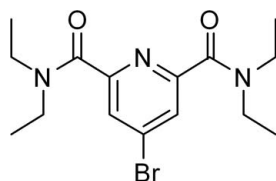
Received 6 July 2010; accepted 19 July 2010

Key indicators: single-crystal X-ray study; *T* = 100 K; mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$; *R* factor = 0.039; *wR* factor = 0.101; data-to-parameter ratio = 17.5.

The title compound, $\text{C}_{15}\text{H}_{22}\text{BrN}_3\text{O}_2$, consists of a pyridine ring with a bromine atom in the *para* position and two diethylamide groups in the *ortho* positions of the ring. Despite the positions of the three substituents on the pyridine ring, the molecule does not exhibit either local or crystallographic twofold symmetry as the two diethylamido units exhibit significantly different $\text{N}_{\text{py}}-\text{C}-\text{C}-\text{N}_{\text{am}}$ torsion angles of $46.3(4)$ and $62.7(4)^\circ$ (py is pyridine and am is amine). Intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions support the packing.

Related literature

The title compound has been investigated as a sensitizer of lanthanide ion luminescence. For uses of this ligand and its derivatives, see: de Bettencourt-Dias *et al.* (2006); Renaud *et al.* (1997). For other structures involving this moiety, see: Muller *et al.* (2003).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{22}\text{BrN}_3\text{O}_2$
 $M_r = 356.27$
 Orthorhombic, *Pbca*

$a = 17.7096(4) \text{ \AA}$
 $b = 8.4987(2) \text{ \AA}$
 $c = 21.5013(4) \text{ \AA}$

$V = 3236.13(12) \text{ \AA}^3$
 $Z = 8$
 Mo $K\alpha$ radiation

$\mu = 2.55 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 $0.17 \times 0.08 \times 0.07 \text{ mm}$

Data collection

Bruker APEX CCD diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 2004)
 $T_{\text{min}} = 0.670$, $T_{\text{max}} = 0.852$

23172 measured reflections
 3392 independent reflections
 2499 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.101$
 $S = 1.05$
 3392 reflections

194 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.56 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.58 \text{ e \AA}^{-3}$

Table 1

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

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C2—H2···O1 ⁱ	0.95	2.54	3.429 (4)	156
C8—H8A···O2 ⁱⁱ	0.99	2.59	3.250 (4)	124
C9—H9A···O1 ⁱⁱⁱ	0.98	2.48	3.447 (4)	168
C9—H9B···O2 ⁱⁱ	0.98	2.87	3.479 (4)	121
C10—H10A···O1 ⁱⁱⁱ	0.99	2.72	3.652 (4)	157
C13—H13A···O2 ^{iv}	0.99	2.63	3.415 (4)	135
C14—H14A···O2 ^{iv}	0.99	2.73	3.444 (4)	130
C15—H15A···O2 ^{iv}	0.98	2.99	3.525 (4)	115

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

The authors thank the University of Nevada, Reno and the National Science Foundation (CHE-0733458) for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2308).

References

- Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Bruker (2001). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
 de Bettencourt-Dias, A. & Poloukhina, A. (2006). *J. Phys. Chem. B*, **110**, 25638–25645.
 Muller, G., Schmidt, B., Jiříček, J., Bünzli, J.-C. G. & Schenk, K. J. (2003). *Acta Cryst. C* **59**, o353–o356.
 Renaud, F., Piguet, C., Bernardinelli, G. & Bünzli, J.-C. G. (1997). *Chem. Eur. J.* **3**, 1646–1659.
 Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.

supplementary materials

Acta Cryst. (2010). E66, o2124 [doi:10.1107/S1600536810028837]

4-Bromo- N^2,N^2,N^6,N^6 -tetraethylpyridine-2,6-dicarboxamide

D. T. de Lill and A. de Bettencourt-Dias

Comment

The title compound, shown in Figure 1 and Scheme 1, is often utilized as the chelating and sensitizing moiety in ligands for lanthanide ion luminescent complexes, such as in (*tert*-butoxycarbonyl) alanine methyl ester, the structure of which has been reported (Muller *et al.*, 2003) or in a N,N,N',N' -tetraethylpyridine-2,6-dicarboxamide-based ligand (Renaud *et al.*, 1997). It has also been used as an intermediate to ligands capable of coordinating lanthanide ions (de Bettencourt-Dias *et al.*, 2006) and as such was isolated in our research group. It consists of a pyridine ring with a bromide in position 4 and diethylamide groups in positions 2 and 5. This molecule is devoid of crystallographic symmetry and the asymmetric unit comprises one molecule. While at first impression the amide groups seem to be related by a twofold axis, closer inspection shows that they are different. This is evidenced by the torsion angles between the groups and the pyridine ring. The torsion angle for the atoms N1—C1—C7—N2 is 62.7 (4)° and the torsion angle for N1—C5—C6—N3 is 46.3 (4)°. The observed difference between the two ethyl groups might be a consequence of the C—H···O hydrogen bond interactions in which they are involved and which help support the packing structure, shown in Figure 2. Despite the presence of the pyridine rings and of the bromine atoms, π - π , C—Br··· π or C—H···Br interactions are not observed.

Experimental

The title compound was synthesized as follows. PBr_5 was obtained by slowly adding 8 ml of PBr_3 to 3.5 ml of Br_2 in 20 ml hexanes at 0 °C. After one hour, the hexanes were decanted and 5 g of chelidamic acid were added. The mixture was heated for six hours (85–90 °C.) The acid bromide which formed in this step was then extracted with chloroform and used without further purification in the next step.

The solution of the acid bromide in $CHCl_3$ was slowly added to 2-chlorodiethylamine (2 eq.) in 50 ml H_2O/KOH (5 eq.) at 0 °C, stirred for 20 minutes, then allowed to slowly warm to room temperature. The aqueous layer was washed and discarded. The organic layer was concentrated, filtered, and the product rinsed with water and hexanes. Crystals were grown by allowing a solution of (I) in $CHCl_3$ to evaporate overnight. Overall yield: 5.7 g, 59%. 1H NMR (400 MHz, $CDCl_3$) p.p.m.: 7.80 (m, 2H), 3.55 (q, 4H), 3.33 (q, 4H), 1.25 (t, 6H), 1.15 (dd, 6H).

Refinement

Hydrogen atoms were positioned geometrically using a riding model with C—H = 0.95, 0.99 and 0.98 Å for aromatic CH and aliphatic CH_2 and CH_3 H atoms, respectively, and $U_{iso}(H)=1.2-1.5 U_{eq}(C)$.

Figures

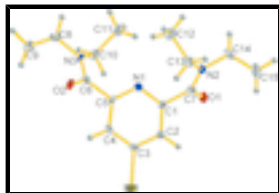


Fig. 1. Molecular structure of the title compound, with atom numbering (except H atoms) and 50% probability displacement ellipsoids for non-H atoms.

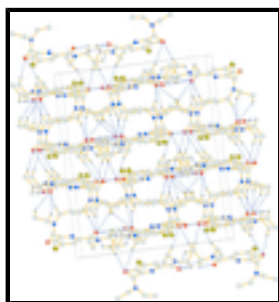


Fig. 2. Packing diagram of the title compound viewed down the *b* axis. The hydrogen bonds are drawn as dashed lines. Hydrogen atoms not involved in hydrogen bonding interactions were omitted for clarity.

4-Bromo-*N*²,*N*²,*N*⁶,*N*⁶-tetraethylpyridine-2,6- dicarboxamide

Crystal data

$C_{15}H_{22}BrN_3O_2$

$M_r = 356.27$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 17.7096$ (4) Å

$b = 8.4987$ (2) Å

$c = 21.5013$ (4) Å

$V = 3236.13$ (12) Å³

$Z = 8$

$F(000) = 1472$

$D_x = 1.462$ Mg m⁻³

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

Cell parameters from 4936 reflections

$\theta = 2.8$ – 27.8°

$\mu = 2.55$ mm⁻¹

$T = 100$ K

Needle, clear light yellow

$0.17 \times 0.08 \times 0.07$ mm

Data collection

Bruker APEX CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

phi and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2004)

$T_{\min} = 0.670$, $T_{\max} = 0.852$

23172 measured reflections

3392 independent reflections

2499 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\max} = 26.7^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -22 \rightarrow 16$

$k = -10 \rightarrow 10$

$l = -26 \rightarrow 27$

Refinement

Refinement on F^2

Primary atom site location: structure-invariant direct
methods

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.039$$

$$wR(F^2) = 0.101$$

$$S = 1.05$$

3392 reflections

194 parameters

0 restraints

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 6.2825P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.58 \text{ e } \text{\AA}^{-3}$$

Special details

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.122569 (19)	0.65446 (4)	0.436078 (17)	0.02253 (12)
N1	0.02418 (15)	0.1655 (3)	0.38110 (12)	0.0146 (6)
C2	0.13042 (19)	0.3352 (4)	0.39707 (14)	0.0152 (7)
H2	0.1835	0.3507	0.3959	0.018*
C6	-0.10501 (18)	0.2584 (4)	0.39805 (14)	0.0157 (7)
C3	0.08262 (19)	0.4540 (4)	0.41694 (15)	0.0166 (7)
C4	0.00592 (19)	0.4288 (4)	0.41939 (14)	0.0164 (7)
H4	-0.0277	0.5091	0.4327	0.020*
C5	-0.02047 (17)	0.2821 (4)	0.40168 (14)	0.0126 (6)
C1	0.09906 (18)	0.1947 (4)	0.37915 (14)	0.0133 (7)
C7	0.14800 (18)	0.0595 (4)	0.35846 (15)	0.0165 (7)
C9	-0.26126 (18)	0.1403 (4)	0.46580 (16)	0.0214 (8)
H9A	-0.2419	0.0830	0.5020	0.032*
H9B	-0.3144	0.1130	0.4592	0.032*
H9C	-0.2568	0.2538	0.4731	0.032*
C15	0.2606 (2)	-0.0792 (5)	0.25542 (17)	0.0318 (10)
H15A	0.2525	-0.0110	0.2193	0.048*
H15B	0.2899	-0.1718	0.2428	0.048*
H15C	0.2885	-0.0212	0.2874	0.048*
C14	0.1854 (2)	-0.1311 (4)	0.28117 (17)	0.0261 (8)
H14A	0.1579	-0.1914	0.2490	0.031*
H14B	0.1939	-0.2017	0.3171	0.031*
C13	0.0897 (2)	0.0736 (4)	0.25344 (16)	0.0226 (8)

supplementary materials

H13A	0.1166	0.0742	0.2131	0.027*
H13B	0.0794	0.1843	0.2650	0.027*
C8	-0.21630 (18)	0.0963 (4)	0.40922 (16)	0.0194 (7)
H8A	-0.2251	-0.0161	0.3996	0.023*
H8B	-0.2343	0.1591	0.3734	0.023*
C11	-0.0732 (2)	-0.1413 (4)	0.4195 (2)	0.0338 (10)
H11A	-0.1167	-0.1810	0.3961	0.051*
H11B	-0.0557	-0.2222	0.4486	0.051*
H11C	-0.0324	-0.1150	0.3905	0.051*
C10	-0.0960 (2)	0.0050 (4)	0.45545 (17)	0.0218 (8)
H10A	-0.1294	-0.0264	0.4902	0.026*
H10B	-0.0502	0.0534	0.4736	0.026*
C12	0.0153 (2)	-0.0114 (5)	0.24541 (19)	0.0371 (10)
H12A	0.0249	-0.1224	0.2358	0.056*
H12B	-0.0131	0.0368	0.2113	0.056*
H12C	-0.0140	-0.0037	0.2839	0.056*
N3	-0.13501 (14)	0.1225 (3)	0.41736 (13)	0.0139 (6)
N2	0.13906 (15)	0.0027 (3)	0.30094 (12)	0.0172 (6)
O2	-0.14317 (12)	0.3659 (3)	0.37517 (11)	0.0202 (5)
O1	0.19438 (13)	0.0070 (3)	0.39535 (10)	0.0209 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0197 (2)	0.01536 (18)	0.0325 (2)	-0.00308 (14)	0.00063 (16)	-0.00522 (15)
N1	0.0166 (14)	0.0131 (13)	0.0141 (13)	-0.0011 (11)	0.0015 (11)	0.0005 (11)
C2	0.0151 (17)	0.0178 (16)	0.0127 (15)	-0.0028 (14)	-0.0021 (13)	0.0008 (13)
C6	0.0174 (17)	0.0162 (16)	0.0135 (16)	0.0016 (14)	0.0000 (14)	-0.0022 (13)
C3	0.0200 (18)	0.0113 (16)	0.0185 (17)	-0.0017 (14)	-0.0041 (14)	-0.0008 (13)
C4	0.0178 (18)	0.0156 (16)	0.0157 (16)	0.0031 (14)	0.0034 (14)	-0.0007 (13)
C5	0.0079 (15)	0.0167 (16)	0.0131 (16)	0.0002 (13)	-0.0003 (13)	0.0027 (13)
C1	0.0127 (16)	0.0161 (16)	0.0111 (15)	-0.0004 (13)	-0.0018 (13)	-0.0003 (12)
C7	0.0169 (17)	0.0138 (16)	0.0186 (17)	-0.0028 (13)	0.0022 (14)	0.0010 (13)
C9	0.0112 (18)	0.0279 (19)	0.0252 (18)	-0.0027 (14)	-0.0031 (15)	0.0034 (16)
C15	0.033 (2)	0.037 (2)	0.026 (2)	0.0149 (19)	0.0127 (17)	0.0035 (17)
C14	0.036 (2)	0.0167 (18)	0.0251 (19)	0.0075 (16)	0.0013 (17)	-0.0057 (15)
C13	0.020 (2)	0.028 (2)	0.0197 (18)	0.0047 (16)	-0.0041 (15)	-0.0047 (15)
C8	0.0145 (17)	0.0184 (16)	0.0253 (18)	-0.0045 (14)	-0.0016 (15)	0.0007 (15)
C11	0.022 (2)	0.0176 (18)	0.062 (3)	0.0013 (15)	0.013 (2)	0.0019 (18)
C10	0.0134 (17)	0.0191 (17)	0.033 (2)	0.0004 (14)	-0.0016 (15)	0.0082 (15)
C12	0.026 (2)	0.055 (3)	0.030 (2)	-0.003 (2)	-0.0050 (18)	-0.016 (2)
N3	0.0051 (13)	0.0152 (14)	0.0213 (14)	-0.0007 (10)	0.0014 (11)	0.0023 (11)
N2	0.0154 (15)	0.0169 (14)	0.0192 (15)	0.0034 (11)	-0.0015 (12)	-0.0030 (12)
O2	0.0104 (11)	0.0212 (13)	0.0291 (13)	0.0022 (9)	0.0010 (10)	0.0068 (10)
O1	0.0163 (12)	0.0237 (13)	0.0228 (13)	0.0049 (10)	-0.0011 (11)	-0.0005 (10)

Geometric parameters (\AA , $^\circ$)

Br1—C3	1.890 (3)	C15—H15C	0.9800
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N1—C5	1.343 (4)	C14—N2	1.465 (4)
N1—C1	1.350 (4)	C14—H14A	0.9900
C2—C1	1.372 (4)	C14—H14B	0.9900
C2—C3	1.385 (4)	C13—N2	1.474 (4)
C2—H2	0.9500	C13—C12	1.512 (5)
C6—O2	1.238 (4)	C13—H13A	0.9900
C6—N3	1.338 (4)	C13—H13B	0.9900
C6—C5	1.513 (4)	C8—N3	1.467 (4)
C3—C4	1.376 (5)	C8—H8A	0.9900
C4—C5	1.385 (4)	C8—H8B	0.9900
C4—H4	0.9500	C11—C10	1.519 (5)
C1—C7	1.506 (4)	C11—H11A	0.9800
C7—O1	1.226 (4)	C11—H11B	0.9800
C7—N2	1.337 (4)	C11—H11C	0.9800
C9—C8	1.501 (5)	C10—N3	1.465 (4)
C9—H9A	0.9800	C10—H10A	0.9900
C9—H9B	0.9800	C10—H10B	0.9900
C9—H9C	0.9800	C12—H12A	0.9800
C15—C14	1.509 (5)	C12—H12B	0.9800
C15—H15A	0.9800	C12—H12C	0.9800
C15—H15B	0.9800		
C5—N1—C1	116.9 (3)	C15—C14—H14B	109.2
C1—C2—C3	118.2 (3)	H14A—C14—H14B	107.9
C1—C2—H2	120.9	N2—C13—C12	113.6 (3)
C3—C2—H2	120.9	N2—C13—H13A	108.8
O2—C6—N3	122.9 (3)	C12—C13—H13A	108.8
O2—C6—C5	117.6 (3)	N2—C13—H13B	108.8
N3—C6—C5	119.5 (3)	C12—C13—H13B	108.8
C4—C3—C2	120.2 (3)	H13A—C13—H13B	107.7
C4—C3—Br1	120.1 (2)	N3—C8—C9	112.7 (3)
C2—C3—Br1	119.7 (2)	N3—C8—H8A	109.1
C3—C4—C5	117.5 (3)	C9—C8—H8A	109.1
C3—C4—H4	121.2	N3—C8—H8B	109.1
C5—C4—H4	121.2	C9—C8—H8B	109.1
N1—C5—C4	123.8 (3)	H8A—C8—H8B	107.8
N1—C5—C6	117.9 (3)	C10—C11—H11A	109.5
C4—C5—C6	117.9 (3)	C10—C11—H11B	109.5
N1—C1—C2	123.3 (3)	H11A—C11—H11B	109.5
N1—C1—C7	115.7 (3)	C10—C11—H11C	109.5
C2—C1—C7	120.9 (3)	H11A—C11—H11C	109.5
O1—C7—N2	123.1 (3)	H11B—C11—H11C	109.5
O1—C7—C1	118.2 (3)	N3—C10—C11	113.5 (3)
N2—C7—C1	118.7 (3)	N3—C10—H10A	108.9
C8—C9—H9A	109.5	C11—C10—H10A	108.9
C8—C9—H9B	109.5	N3—C10—H10B	108.9
H9A—C9—H9B	109.5	C11—C10—H10B	108.9
C8—C9—H9C	109.5	H10A—C10—H10B	107.7
H9A—C9—H9C	109.5	C13—C12—H12A	109.5
H9B—C9—H9C	109.5	C13—C12—H12B	109.5

supplementary materials

C14—C15—H15A	109.5	H12A—C12—H12B	109.5
C14—C15—H15B	109.5	C13—C12—H12C	109.5
H15A—C15—H15B	109.5	H12A—C12—H12C	109.5
C14—C15—H15C	109.5	H12B—C12—H12C	109.5
H15A—C15—H15C	109.5	C6—N3—C8	118.9 (3)
H15B—C15—H15C	109.5	C6—N3—C10	125.1 (3)
N2—C14—C15	112.0 (3)	C8—N3—C10	115.2 (3)
N2—C14—H14A	109.2	C7—N2—C14	118.8 (3)
C15—C14—H14A	109.2	C7—N2—C13	124.3 (3)
N2—C14—H14B	109.2	C14—N2—C13	116.7 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 \cdots O1 ⁱ	0.95	2.54	3.429 (4)	156
C8—H8A \cdots O2 ⁱⁱ	0.99	2.59	3.250 (4)	124
C8—H8B \cdots O2	0.99	2.39	2.732 (4)	100
C9—H9A \cdots O1 ⁱⁱⁱ	0.98	2.48	3.447 (4)	168
C9—H9B \cdots O2 ⁱⁱ	0.98	2.87	3.479 (4)	121
C10—H10A \cdots O1 ⁱⁱⁱ	0.99	2.72	3.652 (4)	157
C13—H13A \cdots O2 ^{iv}	0.99	2.63	3.415 (4)	135
C14—H14A \cdots O2 ^{iv}	0.99	2.73	3.444 (4)	130
C15—H15A \cdots O2 ^{iv}	0.98	2.99	3.525 (4)	115

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

Fig. 1

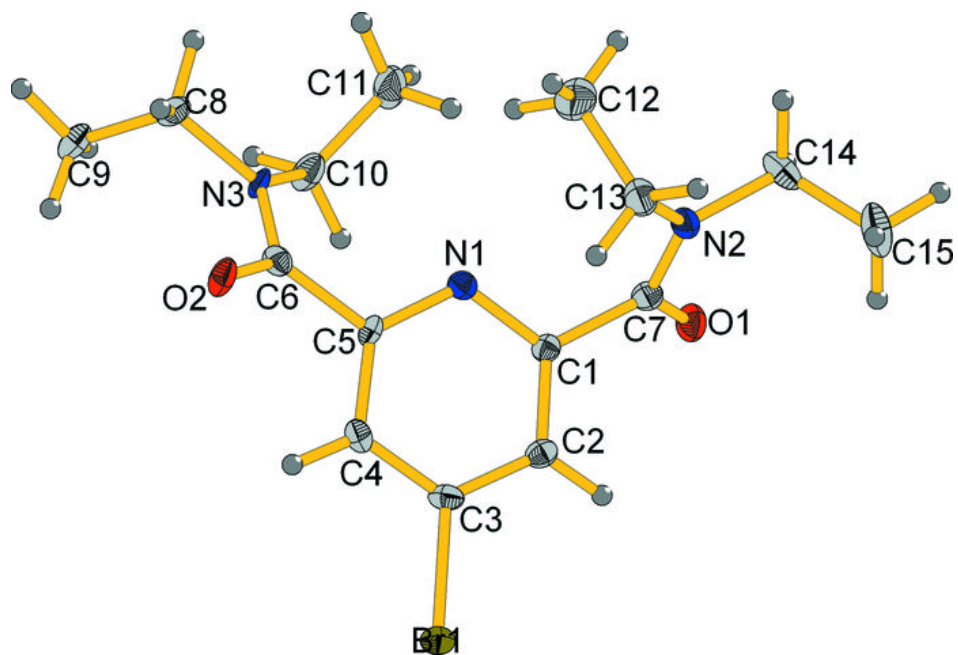


Fig. 2

