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Two isostructural carbamates: the *o*-tolyl *N*-(pyridin-3-yl)carbamate and 2-bromophenyl *N*-(pyridin-3-yl)carbamate monohydrates

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The title carbamate monohydrates, $C_{13}H_{12}N_2O_2 \cdot H_2O$ and $C_{12}H_9BrN_2O_2 \cdot H_2O$, form isomorphous crystals that are isostructural in their primary hydrogen-bonding modes. In both carbamates, the primary hydrogen bonding and aggregation involves cyclic amide–water–pyridine moieties as $(N-H \cdots O-H \cdots N)_2$ dimers about inversion centres [as $R_4^4(14)$ rings], where the participation of strong hydrogen-bonding donors and acceptors is maximized. The remaining water–carbonyl $O-H \cdots O=C$ interaction extends the aggregation into two-dimensional planar sheets that stack parallel to the (100) plane. The Br derivative does not participate in halogen bonding. A weak intramolecular $C-H \cdots O$ hydrogen bond is observed in each compound.

1. Chemical context

Isomorphous crystals and isostructural compounds feature regularly in series of metalloorganic compounds, lanthanide derivatives as well as in halide-containing organics (*RX*, where *X* = F, Cl, Br, I and often including the methyl group, Me). Given the vast array of data available in the Cambridge Structural Database (CSD; Groom & Allen, 2014), the relative proportion of isostructural relationships between sets of crystal structures can readily be ascertained. As such, Oswald & Crichton (2009) have reported on the regularity with which chlorine (Cl) and methyl (Me) groups exhibit isostructurality based on analysis of pairs of compounds in the CSD (van de Streek & Motherwell, 2005), whereby an estimate of 25–30% of compound pairs are isostructural. In addition, Polito *et al.* (2008) have rationalized the differences and similarities between *ortho*-chloro and *ortho*-methylbenzoic acids, while the ability of bromines (as Br—C) as well as other halogens to form isostructural pairs/series with methyl groups is well documented (Capacci-Daniel *et al.*, 2008).

These researchers have reported an elegant example of an isostructural series of 1,3-bis(*meta*-dihalophenyl)ureas (with halo = Cl, Br, I) that form isomorphous crystals in space group $P2_12_12_1$ (No. 18) and reported with mono- and di-tolyl analogues (Capacci-Daniel *et al.*, 2008). The molecules associate *via* $(N-H)_2 \cdots O=C$ interactions into 1D chains [$R_6^1(6)$ motif] and with $\pi-\pi$ stacking interactions and halogen contacts completing the aggregation. One can surmise that isostructural series in organic molecules are possible whereby 1-2 strong hydrogen bonds dominate the interactions and drive molecular association, despite often semi-effective cumulative competition from other interactions, whilst taking into account the effect of atom/group replacement (Groom & Allen, 2014).

Further examples in coordination chemistry include the halogen-substituted pseudoterpyridine Zn^{II} homoleptic

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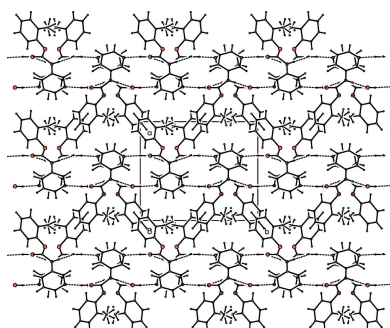
mononuclear complexes that lack strong hydrogen bonding and with the packing relying on a subtle interplay of weaker interactions, where isostructurality is rare amongst the four (F/Cl/Br/I) halogens (Dumitru *et al.*, 2013). Another example is where the metal complexes (Co[II], Ni[II], Cu[II], Zn[II]) form an isostructural series when coordinated to a tetraarylaza-dipyrromethene ligand (Palma *et al.*, 2009). The interchangeability effects of C—H and C—F groups in series of isomeric fluorinated benzamides has been noted (Chopra & Guru Row, 2008; Donnelly *et al.*, 2008) and for C—H/C—CH$_3$ (Mocilac *et al.*, 2010). More recently, Gomes and co-workers have reported four *N*-(4-halophenyl)-4-oxo-4*H*-chromene-3-carboxamides (halo = F/Cl/Br/I), where isostructural (F/Cl) and (Br/I) pairs are noted though all four compounds have similar supramolecular structures (Gomes *et al.*, 2015).
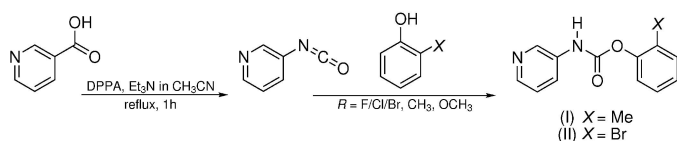
2. Structural commentary

The carbamates synthesised from condensation reactions (shown in the scheme) as their methyl (**CmoM**) and bromo-derivatives (**CmoBr**) crystallize as isostructural monohydrates. The differences between the unit-cell parameters (*a*, *b*, *c*, *β*) are < 1% for **CmoM** (I) and **CmoBr** (II). Both molecules have similar geometric data (bond lengths and angles) apart from the (*ortho*)C—CH$_3$/Br bond-length differences and some interplanar data. The molecules have three primary torsion angles along the molecular backbone namely $_{benzene}$C—C—O—C, C—O—C—N and C—N—C—C$_{pyridine}$ where the molecule can adopt one of several conformations in solution. In (I) and (II), both aromatic rings are twisted from co-planarity with the four-membered OCON non-H carbamate atom backbone. The **CmoM** C$_6$ ring is oriented at an angle of 87.83 (4)° to the central carbamate moiety which lies at an angle of 25.79 (7)° to the C$_5$N ring; the corresponding data for **CmoBr** are 88.60 (11) and 26.67 (18)° and highlighting the

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O1W	0.875 (16)	1.953 (16)	2.8274 (14)	179.1 (15)
O1W—H1W⋯O1^i	0.85 (2)	2.06 (2)	2.9126 (15)	173.2 (18)
O1W—H2W⋯N23^{ii}	0.86 (2)	1.97 (3)	2.8266 (16)	170.6 (19)
C26—H26⋯O1	0.93	2.43	2.9337 (15)	114

Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x + 1, -y + 2, -z$.

Table 2
Hydrogen-bond geometry (Å, °) for **CmoBr**.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O1W	0.74 (3)	2.10 (3)	2.832 (4)	177 (3)
O1W—H1W⋯O1^i	0.75 (4)	2.18 (5)	2.924 (4)	177 (5)
O1W—H2W⋯N23^{ii}	0.71 (4)	2.13 (4)	2.837 (4)	175 (4)
C26—H26⋯O1	0.93	2.44	2.946 (4)	114

Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x + 1, -y + 2, -z$.

similarities in the two molecular structures. For comparison, we have previously reported an isomer grid of nine related methoxycarbamates (**C*xx*OMe**) (*x* = *ortho-*/*meta-*/*para-*) in order to compare their crystal structures and molecular models (Mocilac & Gallagher, 2013).

In the **C*xx*OMe** series (Mocilac & Gallagher, 2013), the primary interaction mode for all nine isomers is the amide⋯pyridine (as N—H⋯N) and typically aggregating as catemers, dimers or trimers. However, there is no evidence for the familiar N—H⋯O=C (amide⋯amide) type hydrogen bonding (Mocilac & Gallagher, 2013). This is in comparison to a series of related benzamides/carboxamides containing one strong donor/two strong acceptors where competition arises resulting in the formation of either (i) N—H⋯N or (ii) N—H⋯O=C hydrogen bonds as the primary strong interaction (Mocilac *et al.*, 2010, 2012). In the title structures of **CmoM** (Fig. 1) and **CmoBr** (Fig. 2), the presence of a water molecule in the asymmetric unit was unexpected (water typically assists in the decomposition of organic carbamates at room temperature) though it can be shown to confer additional stability on the structure by forming compact hydrogen
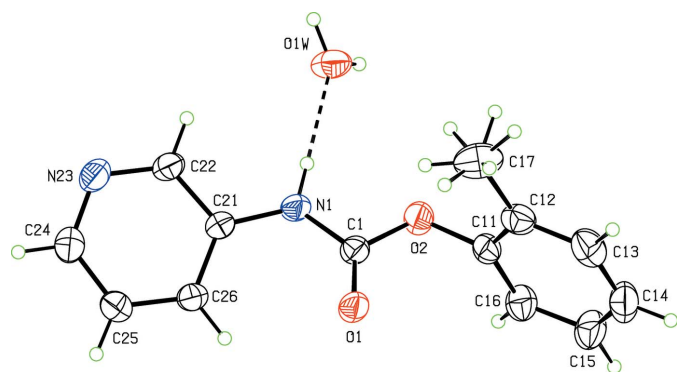

Figure 1
View of the asymmetric unit of (I)·H$_2$O, showing the atomic numbering schemes. Rotational disorder of the methyl group is depicted. Displacement ellipsoids are drawn at the 30% probability level.
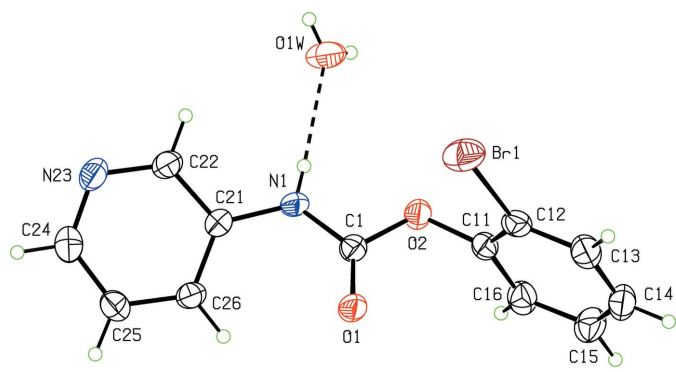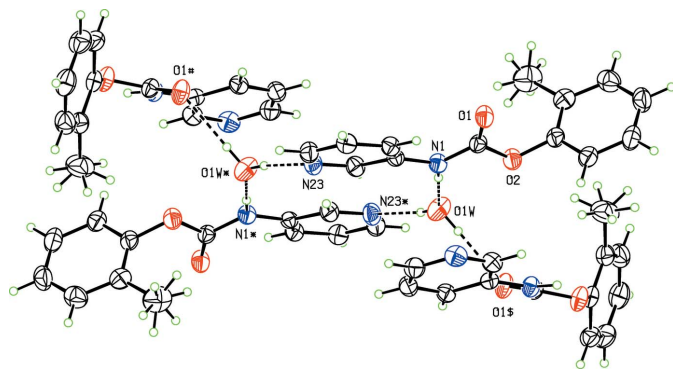

Figure 2
View of the asymmetric unit of (II)·H$_2$O, showing the atomic numbering schemes. Displacement ellipsoids are drawn at the 30% probability level.
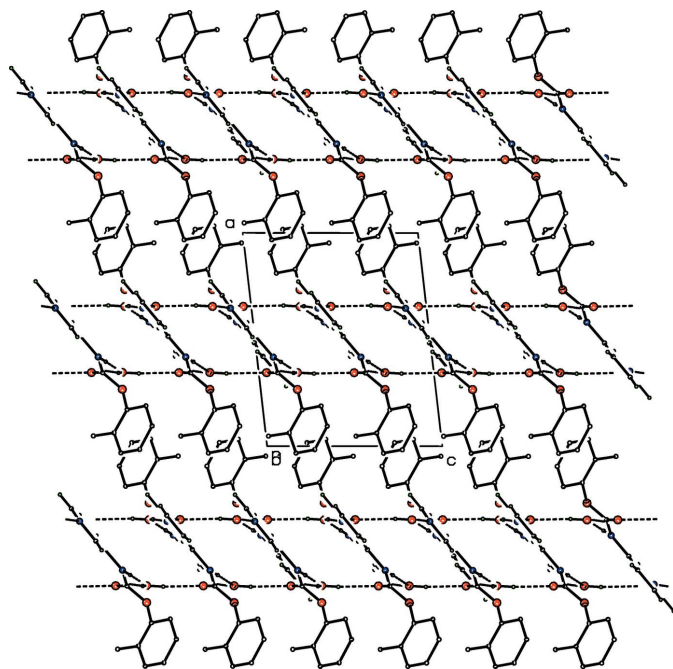
Figure 3
Part of the crystal structure of (I) with the primary interactions as a hydrogen-bonded moiety of four carbamates surrounding two hydrogen-bonded water molecules and with selected labels. The symmetry-related molecules with suffices *, #, $ are positioned at $(1 - x, 2 - y, -z)$, $(1 - x, \frac{1}{2} + y, -\frac{1}{2} - z)$ and $(x, \frac{3}{2} - y, \frac{1}{2} + z)$, respectively.

bonding and contributing to sheet formation. The retention of carbamate crystal structure integrity is observed over time (as measured in months).

3. Supramolecular features

The three primary hydrogen bonds in (I) and (II) as N1—H1···O1W, O1W—H1W···O1 and O1W—H2W···N23 (Tables 1 and 2) are classed as strong classical hydrogen bonds with donor–acceptor $(D···A)$ distances < 2.95 Å and D—H···A angles close to linearity at 180°. In Figs. 3–5 the crystal packing and interactions for **CmoM** are shown and in general

Figure 4
A packing diagram of the two-dimensional sheets and interlocking o-tolyl groups in **CmoM** (with aromatic C_6 H atoms removed for clarity). Atoms are drawn as spheres of an arbitrary size.
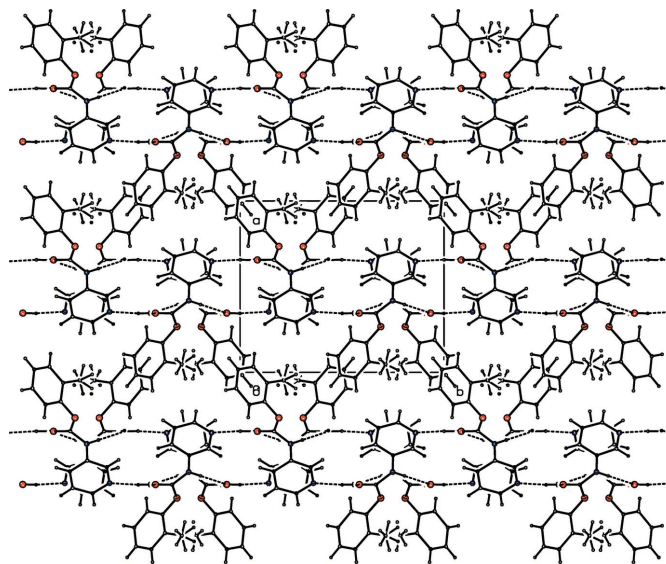
Figure 5
A packing diagram of **CmoM** as two-dimensional sheets as viewed orthogonal to the direction shown in Fig. 4. Atoms are drawn as spheres of an arbitrary size with all H atoms included.

are similar for **CmoBr**. The amide···water···pyridine hydrogen bonds facilitate aggregation of a centrosymmetric ring of hydrogen bonds [as $R_4^4(14)$ rings] (Fig. 3) which, when combined with the water···amide carbonyl (O=C) inter-action, generates a compact flattened 2D sheet of hydrogen bonds that lies parallel to the (100) plane (Figs. 4 and 5). The hydrogen bonding intercepts the a-axis at 0.33 and 0.67 along the unit-cell axis and the sheet is a unit-cell length (a) in thickness with hydrophobic aromatic rings at the 2D sheet surfaces. The 3D crystal structure arises where 2D sheets stack parallel to the a-axis direction.

4. Synthesis and crystallisation

Carbamate formation (**CmoX**; **X** = Me, Br): The simplest method of phenyl-N-pyridinyl-carbamate (**CxxR**) synthesis is a condensation reaction of aminopyridines with commercially available phenylchloroformates in the presence of base (Et₃N) and solvent (CH₂Cl₂). This is performed in an analogous fashion to the Schotten–Baumann reaction and can provide relatively pure products in high yields. However, when using 2-aminopyridines, additional double carbamates are formed where both of the N—H H atoms are replaced by formates. In order to minimize double carbamate formation for these derivatives, reactions are usually performed by mixing the reagents without solvent and base at lower temperature, followed by simple recrystallization.

Another viable route into carbamate chemistry is to use an agent that transforms phenols into the required chloroformate; however, a simpler and more straightforward method for carbamate synthesis is the Curtius rearrangement reaction (or Curtius reaction or degradation) involving the rearrangement of an acyl azide to an isocyanate. The acyl azide (in this case pyridinyl azide) can be formed from the carboxylic

Table 3
Experimental details.

	CmoM	CmoBr
Crystal data		
Chemical formula	$C_{13}H_{12}N_2O_2 \cdot H_2O$	$C_{12}H_9BrN_2O_2 \cdot H_2O$
M_r	246.26	311.14
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	294	294
a, b, c (Å)	10.9754 (2), 12.9877 (2), 8.9544 (2)	10.9036 (4), 13.0518 (3), 8.9804 (3)
β (°)	96.546 (2)	96.460 (3)
V (Å^3)	1268.09 (4)	1269.90 (7)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.09	3.24
Crystal size (mm)	$0.61 \times 0.36 \times 0.19$	$0.35 \times 0.20 \times 0.04$
Data collection		
Diffractometer	Agilent Xcalibur Sapphire3 Gemini Ultra	Agilent Xcalibur Sapphire3 Gemini Ultra
Absorption correction	Analytical (*ABSFAC*; Clark & Reid, 1998)	Analytical (*ABSFAC*; Clark and Reid, 1998)
T_{min}, T_{max}	0.962, 0.983	0.398, 0.844
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14095, 4060, 2987	9904, 2811, 1881
R_{int}	0.017	0.029
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.739	0.658
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.136, 1.03	0.046, 0.106, 1.03
No. of reflections	4060	2811
No. of parameters	177	175
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.21, −0.16	0.68, −0.64

Computer programs: *CrysAlis PRO* (Agilent, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

acid by a suitable agent like diphenylphosphoryl azide. The acid can be easily converted to pyridinyl azides using diphenylphosphoryl azide and at higher temperature (343 K) in the presence of base. The pyridinyl azides rearrange into pyridinyl isocyanates and following reaction with a phenol, the required phenyl-*N*-pyridinyl-carbamate (**CxxR**) is generated.

Reaction procedure: A mixture of isonicotinic acid (1.2877 g, 10.46 mmol), Et$_3$N (1.46 ml, 10.46 mmol), and diphenylphosphoryl azide (2.258 ml, 10.46 mmol) was stirred for 1 h in 30 mL of dry acetonitrile at room temperature. The reaction mixture was carefully heated (water bath) to reflux for 1 h, then with 2-methylphenol or 2-bromophenol (10.46 mmol) added and the resulting solution heated at reflux temperatures for 7 h, gradually cooled and stirred overnight. If a white precipitate formed, it was filtered, washed with acetonitrile and dried (and usually found to be the pure product). The solvent was removed from the reaction mixture under reduced pressure, the residue dissolved in CH$_2$Cl$_2$, washed thrice with a solution of KHCO$_3$ and Na$_2$CO$_3$ (pH = 9) and twice with brine/ammonium chloride (pH = 5). The organic fraction was removed *in vacuo* and the compound recrystallized from diethyl ether and CH$_2$Cl$_2$. If necessary, purification was accomplished by column chromatography using silica as the stationary phase and a mixture of CH$_2$Cl$_2$ and methanol (8:1) as mobile phase. Both **ComM** (46% yield, m.p. range = 352–357 K) and **ComBr** (21% yield, m.p. range = 359.2–359.9 K) compounds were obtained using this method (Mocilac, 2012).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The refinement of structures (I) and (II) were performed similarly. H atoms attached to C atoms were treated as riding using the *SHELXL2014* (Sheldrick, 2015) defaults at 294 (1) K with C—H = 0.93 Å (aromatic) and U_{iso}(H) = $1.2U_{eq}$(C) (aromatic). The methyl C—H = 0.96 Å (aliphatic) and U_{iso}(H) = $1.5U_{eq}$(C). The amino N—H and water O—H H atoms were refined with isotropic displacement parameters in both structures (I) and (II). In (I) the methyl group H atoms were refined as disordered over two sets of sites with equal occupancies 60° apart.

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supporting information

Two isostructural carbamates: the *o*-tolyl *N*-(pyridin-3-yl)carbamate and 2-bromophenyl *N*-(pyridin-3-yl)carbamate monohydrates

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Computing details

For both compounds, data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

(CmoM) 2-Methylphenyl *N*-(pyridin-3-yl)carbamate monohydrate

Crystal data

$C_{13}H_{12}N_2O_2 \cdot H_2O$	$D_x = 1.290$ Mg m^{-3}
$M_r = 246.26$	Melting point: 355 K
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.9754$ (2) Å	Cell parameters from 6097 reflections
$b = 12.9877$ (2) Å	$\theta = 2.4–31.5°$
$c = 8.9544$ (2) Å	$\mu = 0.09$ mm^{-1}
$\beta = 96.546$ (2)°	$T = 294$ K
$V = 1268.09$ (4) Å^3	Block, colourless
$Z = 4$	$0.61 \times 0.36 \times 0.19$ mm
$F(000) = 520$	

Data collection

Agilent Xcalibur Sapphire3 Gemini Ultra diffractometer	2987 reflections with $I > 2\sigma(I)$
Radiation source: Enhance (Mo) X-ray Source	$R_{int} = 0.017$
ω scans	$\theta_{max} = 31.7°$, $\theta_{min} = 2.4°$
Absorption correction: analytical (ABSFAC; Clark & Reid, 1998)	$h = -15 \rightarrow 15$
	$k = -18 \rightarrow 19$
	$l = -12 \rightarrow 12$
$T_{min} = 0.962$, $T_{max} = 0.983$	6097 standard reflections every 60 min
14095 measured reflections	intensity decay: 1%
4060 independent reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	
$wR(F^2) = 0.136$	Hydrogen site location: mixed
$S = 1.03$	H atoms treated by a mixture of independent and constrained refinement
4060 reflections	
177 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.1872P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.21$ e Å^{-3}

$\Delta\rho_{min} = -0.16$ e Å^{-3}

Extinction correction: *SHELXL2014* (Sheldrick, 2015), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$

Extinction coefficient: 0.017 (2)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.34460 (9)	0.58485 (7)	0.04485 (11)	0.0602 (3)	
O2	0.26595 (9)	0.69019 (7)	0.21023 (10)	0.0605 (3)	
N1	0.41760 (10)	0.74813 (7)	0.09353 (12)	0.0489 (2)	
H1	0.3953 (14)	0.8055 (13)	0.1339 (17)	0.064 (4)*	
C1	0.34402 (11)	0.66676 (9)	0.10863 (12)	0.0468 (3)	
C11	0.17108 (12)	0.61974 (9)	0.22454 (13)	0.0507 (3)	
C12	0.06160 (14)	0.63221 (11)	0.13440 (16)	0.0606 (3)	
C13	−0.03242 (14)	0.56479 (14)	0.1608 (2)	0.0744 (4)	
H13	−0.1081	0.5705	0.1030	0.089*	
C14	−0.01636 (16)	0.49030 (14)	0.2696 (2)	0.0774 (5)	
H14	−0.0806	0.4461	0.2844	0.093*	
C15	0.09395 (16)	0.48072 (14)	0.35639 (18)	0.0750 (4)	
H15	0.1048	0.4302	0.4303	0.090*	
C16	0.18854 (14)	0.54588 (12)	0.33415 (15)	0.0623 (3)	
H16	0.2638	0.5400	0.3929	0.075*	
C17	0.0470 (2)	0.71323 (15)	0.0145 (2)	0.0997 (6)	
H17A	−0.0379	0.7320	−0.0053	0.150*	0.5
H17B	0.0751	0.6868	−0.0757	0.150*	0.5
H17C	0.0944	0.7727	0.0477	0.150*	0.5
H17D	0.1256	0.7290	−0.0168	0.150*	0.5
H17E	0.0126	0.7742	0.0535	0.150*	0.5
H17F	−0.0067	0.6883	−0.0699	0.150*	0.5
C21	0.51507 (11)	0.75035 (8)	0.00573 (12)	0.0429 (2)	
C22	0.55366 (12)	0.84604 (9)	−0.03989 (15)	0.0537 (3)	
H22	0.5115	0.9040	−0.0127	0.064*	
N23	0.64700 (11)	0.85974 (9)	−0.11985 (14)	0.0617 (3)	
C24	0.70646 (13)	0.77623 (12)	−0.15846 (16)	0.0607 (3)	
H24	0.7719	0.7844	−0.2148	0.073*	
C25	0.67509 (12)	0.67857 (11)	−0.11843 (15)	0.0563 (3)	
H25	0.7187	0.6221	−0.1477	0.068*	
C26	0.57875 (11)	0.66476 (9)	−0.03472 (14)	0.0494 (3)	
H26	0.5569	0.5991	−0.0059	0.059*	
O1W	0.34506 (12)	0.93442 (8)	0.22084 (13)	0.0712 (3)	
H1W	0.3406 (17)	0.9329 (15)	0.315 (3)	0.090 (6)*	
H2W	0.3436 (19)	0.9991 (19)	0.199 (2)	0.098 (6)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0760 (6)	0.0421 (4)	0.0675 (6)	−0.0105 (4)	0.0304 (5)	−0.0123 (4)
O2	0.0724 (6)	0.0521 (5)	0.0617 (5)	−0.0120 (4)	0.0284 (4)	−0.0170 (4)
N1	0.0595 (6)	0.0356 (5)	0.0533 (5)	−0.0022 (4)	0.0133 (4)	−0.0054 (4)
C1	0.0567 (7)	0.0414 (5)	0.0437 (5)	−0.0015 (5)	0.0117 (5)	−0.0025 (4)
C11	0.0572 (7)	0.0487 (6)	0.0496 (6)	−0.0016 (5)	0.0207 (5)	−0.0101 (5)
C12	0.0676 (8)	0.0550 (7)	0.0601 (7)	0.0080 (6)	0.0111 (6)	−0.0065 (6)
C13	0.0552 (8)	0.0863 (11)	0.0819 (10)	0.0024 (7)	0.0083 (7)	−0.0138 (9)
C14	0.0702 (10)	0.0854 (11)	0.0825 (11)	−0.0174 (8)	0.0339 (9)	−0.0078 (9)
C15	0.0843 (11)	0.0795 (10)	0.0656 (9)	−0.0082 (8)	0.0276 (8)	0.0120 (8)
C16	0.0634 (8)	0.0722 (9)	0.0528 (7)	−0.0014 (7)	0.0129 (6)	0.0032 (6)
C17	0.1206 (16)	0.0748 (11)	0.0988 (13)	0.0181 (11)	−0.0091 (12)	0.0172 (10)
C21	0.0482 (6)	0.0383 (5)	0.0414 (5)	−0.0027 (4)	0.0020 (4)	0.0006 (4)
C22	0.0605 (7)	0.0393 (6)	0.0615 (7)	−0.0022 (5)	0.0072 (6)	0.0037 (5)
N23	0.0640 (7)	0.0536 (6)	0.0683 (7)	−0.0091 (5)	0.0106 (5)	0.0122 (5)
C24	0.0538 (7)	0.0690 (8)	0.0600 (7)	−0.0046 (6)	0.0103 (6)	0.0062 (6)
C25	0.0521 (7)	0.0564 (7)	0.0606 (7)	0.0061 (5)	0.0074 (5)	−0.0022 (6)
C26	0.0531 (6)	0.0403 (5)	0.0544 (6)	0.0012 (5)	0.0047 (5)	0.0023 (5)
O1W	0.1129 (9)	0.0451 (5)	0.0581 (6)	0.0132 (5)	0.0206 (6)	0.0011 (4)

Geometric parameters (Å, º)

O1—C1	1.2077 (14)	C17—H17B	0.9600
O2—C1	1.3536 (14)	C17—H17C	0.9600
O2—C11	1.4030 (15)	C17—H17D	0.9600
N1—C1	1.3462 (15)	C17—H17E	0.9600
N1—C21	1.3982 (15)	C17—H17F	0.9600
N1—H1	0.875 (16)	C21—C26	1.3832 (16)
C11—C12	1.378 (2)	C21—C22	1.3894 (16)
C11—C16	1.3702 (19)	C22—N23	1.3270 (17)
C12—C13	1.394 (2)	C22—H22	0.9300
C12—C17	1.499 (2)	N23—C24	1.3317 (19)
C13—C14	1.370 (2)	C24—C25	1.373 (2)
C13—H13	0.9300	C24—H24	0.9300
C14—C15	1.368 (3)	C25—C26	1.3757 (18)
C14—H14	0.9300	C25—H25	0.9300
C15—C16	1.371 (2)	C26—H26	0.9300
C15—H15	0.9300	O1W—H1W	0.85 (2)
C16—H16	0.9300	O1W—H2W	0.86 (2)
C17—H17A	0.9600		
C1—O2—C11	116.62 (9)	H17A—C17—H17D	141.1
C1—N1—C21	125.36 (10)	H17B—C17—H17D	56.3
C1—N1—H1	115.3 (10)	H17C—C17—H17D	56.3
C21—N1—H1	118.9 (10)	C12—C17—H17E	109.5
O1—C1—N1	127.48 (11)	H17A—C17—H17E	56.3

O1—C1—O2	123.62 (11)	H17B—C17—H17E	141.1
N1—C1—O2	108.90 (10)	H17C—C17—H17E	56.3
C16—C11—C12	122.90 (13)	H17D—C17—H17E	109.5
C16—C11—O2	118.51 (12)	C12—C17—H17F	109.5
C12—C11—O2	118.45 (12)	H17A—C17—H17F	56.3
C11—C12—C13	116.07 (14)	H17B—C17—H17F	56.3
C11—C12—C17	121.12 (15)	H17C—C17—H17F	141.1
C13—C12—C17	122.80 (16)	H17D—C17—H17F	109.5
C14—C13—C12	121.78 (15)	H17E—C17—H17F	109.5
C14—C13—H13	119.1	C26—C21—C22	117.50 (11)
C12—C13—H13	119.1	C26—C21—N1	124.93 (10)
C15—C14—C13	120.14 (15)	C22—C21—N1	117.52 (10)
C15—C14—H14	119.9	N23—C22—C21	123.96 (12)
C13—C14—H14	119.9	N23—C22—H22	118.0
C14—C15—C16	119.80 (15)	C21—C22—H22	118.0
C14—C15—H15	120.1	C22—N23—C24	117.53 (11)
C16—C15—H15	120.1	N23—C24—C25	122.67 (12)
C11—C16—C15	119.32 (14)	N23—C24—H24	118.7
C11—C16—H16	120.3	C25—C24—H24	118.7
C15—C16—H16	120.3	C24—C25—C26	119.61 (12)
C12—C17—H17A	109.5	C24—C25—H25	120.2
C12—C17—H17B	109.5	C26—C25—H25	120.2
H17A—C17—H17B	109.5	C25—C26—C21	118.72 (11)
C12—C17—H17C	109.5	C25—C26—H26	120.6
H17A—C17—H17C	109.5	C21—C26—H26	120.6
H17B—C17—H17C	109.5	H1W—O1W—H2W	104.2 (18)
C12—C17—H17D	109.5		
C21—N1—C1—O1	−4.1 (2)	C12—C11—C16—C15	0.1 (2)
C21—N1—C1—O2	175.66 (11)	O2—C11—C16—C15	175.69 (12)
C11—O2—C1—O1	−8.96 (18)	C14—C15—C16—C11	−0.1 (2)
C11—O2—C1—N1	171.27 (11)	C1—N1—C21—C26	−24.33 (19)
C1—O2—C11—C16	94.57 (14)	C1—N1—C21—C22	158.06 (12)
C1—O2—C11—C12	−89.69 (14)	C26—C21—C22—N23	0.29 (19)
C16—C11—C12—C13	0.09 (19)	N1—C21—C22—N23	178.08 (12)
O2—C11—C12—C13	−175.46 (11)	C21—C22—N23—C24	0.2 (2)
C16—C11—C12—C17	−179.23 (15)	C22—N23—C24—C25	−0.2 (2)
O2—C11—C12—C17	5.22 (19)	N23—C24—C25—C26	−0.2 (2)
C11—C12—C13—C14	−0.3 (2)	C24—C25—C26—C21	0.63 (19)
C17—C12—C13—C14	178.99 (16)	C22—C21—C26—C25	−0.67 (17)
C12—C13—C14—C15	0.3 (2)	N1—C21—C26—C25	−178.28 (11)
C13—C14—C15—C16	−0.1 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1*W*	0.875 (16)	1.953 (16)	2.8274 (14)	179.1 (15)
O1*W*—H1*W*···O1[i]	0.85 (2)	2.06 (2)	2.9126 (15)	173.2 (18)

| O1W—H2W···N23[ii] | 0.86 (2) | 1.97 (3) | 2.8266 (16) | 170.6 (19) |
| C26—H26···O1 | 0.93 | 2.43 | 2.9337 (15) | 114 |

Symmetry codes: (i) x, $-y+3/2$, $z+1/2$; (ii) $-x+1$, $-y+2$, $-z$.

(CmoBr) 2-Bromophenyl N-(pyridin-3-yl)carbamate monohydrate

Crystal data

$C_{12}H_9BrN_2O_2 \cdot H_2O$	$D_x = 1.627$ Mg m^{-3}
$M_r = 311.14$	Melting point: 359.5 K
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.9036$ (4) Å	Cell parameters from 3330 reflections
$b = 13.0518$ (3) Å	$\theta = 2.3–27.8°$
$c = 8.9804$ (3) Å	$\mu = 3.24$ mm^{-1}
$\beta = 96.460$ (3)°	$T = 294$ K
$V = 1269.90$ (7) Å^3	Plate, colourless
$Z = 4$	$0.35 \times 0.20 \times 0.04$ mm
$F(000) = 624$	

Data collection

Agilent Xcalibur Sapphire3 Gemini Ultra diffractometer	1881 reflections with $I > 2\sigma(I)$
Radiation source: Enhance (Mo) X-ray Source	$R_{int} = 0.029$
ω scans	$\theta_{max} = 27.9°$, $\theta_{min} = 2.4°$
Absorption correction: analytical (ABSFAC; Clark and Reid, 1998)	$h = -13 \rightarrow 11$
	$k = -16 \rightarrow 16$
	$l = -8 \rightarrow 11$
$T_{min} = 0.398$, $T_{max} = 0.844$	3330 standard reflections every 60 min
9904 measured reflections	intensity decay: 1%
2811 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: inferred from neighbouring sites
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.046$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.106$	
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 1.3864P]$ where $P = (F_o^2 + 2F_c^2)/3$
2811 reflections	
175 parameters	$(\Delta/\sigma)_{max} < 0.001$
0 restraints	$\Delta\rho_{max} = 0.68$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.64$ e Å^{-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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.04274 (5)	0.72890 (3)	−0.00738 (5)	0.0794 (2)
O1	0.3437 (2)	0.58402 (17)	0.0455 (3)	0.0543 (6)
O2	0.2663 (2)	0.68665 (17)	0.2147 (3)	0.0514 (6)

N1	0.4156 (3)	0.7464 (2)	0.0937 (3)	0.0447 (7)
H1	0.396 (3)	0.794 (2)	0.127 (3)	0.025 (9)*
C1	0.3436 (3)	0.6650 (2)	0.1092 (4)	0.0423 (7)
C11	0.1718 (3)	0.6166 (2)	0.2272 (4)	0.0444 (8)
C12	0.0609 (3)	0.6262 (2)	0.1409 (4)	0.0490 (9)
C13	−0.0350 (4)	0.5605 (3)	0.1619 (5)	0.0609 (10)
H13	−0.1107	0.5671	0.1037	0.073*
C14	−0.0178 (4)	0.4857 (3)	0.2692 (5)	0.0644 (11)
H14	−0.0820	0.4411	0.2835	0.077*
C15	0.0934 (4)	0.4761 (3)	0.3554 (5)	0.0668 (11)
H15	0.1036	0.4247	0.4273	0.080*
C16	0.1896 (4)	0.5401 (3)	0.3382 (4)	0.0559 (9)
H16	0.2646	0.5335	0.3979	0.067*
C21	0.5132 (3)	0.7507 (2)	0.0050 (3)	0.0398 (7)
C22	0.5498 (3)	0.8458 (3)	−0.0405 (4)	0.0499 (9)
H22	0.5062	0.9029	−0.0134	0.060*
N23	0.6435 (3)	0.8609 (2)	−0.1207 (3)	0.0563 (8)
C24	0.7041 (4)	0.7790 (3)	−0.1586 (4)	0.0584 (10)
H24	0.7698	0.7880	−0.2150	0.070*
C25	0.6750 (3)	0.6817 (3)	−0.1188 (4)	0.0525 (9)
H25	0.7201	0.6262	−0.1479	0.063*
C26	0.5787 (3)	0.6667 (2)	−0.0356 (4)	0.0461 (8)
H26	0.5578	0.6011	−0.0070	0.055*
O1W	0.3476 (3)	0.9335 (2)	0.2214 (4)	0.0694 (9)
H1W	0.345 (4)	0.931 (3)	0.304 (5)	0.071 (16)*
H2W	0.347 (3)	0.986 (3)	0.199 (4)	0.048 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.1013 (4)	0.0583 (3)	0.0771 (3)	0.0123 (2)	0.0035 (3)	0.0144 (2)
O1	0.0693 (17)	0.0377 (13)	0.0605 (15)	−0.0094 (11)	0.0279 (13)	−0.0112 (11)
O2	0.0597 (15)	0.0439 (13)	0.0542 (15)	−0.0133 (11)	0.0228 (12)	−0.0137 (11)
N1	0.0549 (19)	0.0291 (15)	0.0519 (17)	−0.0018 (13)	0.0142 (14)	−0.0053 (12)
C1	0.047 (2)	0.0390 (17)	0.0419 (18)	−0.0009 (15)	0.0090 (15)	0.0001 (14)
C11	0.053 (2)	0.0415 (17)	0.0416 (19)	−0.0033 (15)	0.0190 (17)	−0.0089 (14)
C12	0.062 (2)	0.0411 (18)	0.046 (2)	0.0064 (16)	0.0164 (18)	−0.0038 (14)
C13	0.053 (2)	0.064 (2)	0.067 (3)	−0.0051 (19)	0.015 (2)	−0.013 (2)
C14	0.066 (3)	0.063 (2)	0.070 (3)	−0.017 (2)	0.030 (2)	−0.007 (2)
C15	0.087 (3)	0.061 (2)	0.057 (2)	−0.006 (2)	0.026 (2)	0.0085 (19)
C16	0.055 (2)	0.062 (2)	0.053 (2)	−0.0061 (18)	0.0146 (18)	−0.0086 (18)
C21	0.0423 (18)	0.0383 (18)	0.0381 (16)	−0.0044 (13)	0.0013 (14)	0.0021 (13)
C22	0.052 (2)	0.0381 (18)	0.060 (2)	−0.0024 (15)	0.0055 (18)	0.0043 (15)
N23	0.056 (2)	0.0505 (18)	0.063 (2)	−0.0095 (15)	0.0111 (16)	0.0128 (14)
C24	0.049 (2)	0.070 (3)	0.058 (2)	−0.0043 (19)	0.0125 (18)	0.0058 (19)
C25	0.045 (2)	0.056 (2)	0.057 (2)	0.0053 (17)	0.0091 (17)	−0.0036 (17)
C26	0.050 (2)	0.0353 (17)	0.053 (2)	−0.0005 (15)	0.0047 (17)	0.0022 (14)
O1W	0.116 (3)	0.0386 (16)	0.056 (2)	0.0123 (16)	0.0216 (19)	0.0024 (14)

Geometric parameters (Å, º)

Br1—C12	1.884 (3)	C15—H15	0.9300
O1—C1	1.201 (4)	C16—H16	0.9300
O2—C1	1.367 (4)	C21—C22	1.380 (4)
O2—C11	1.391 (4)	C21—C26	1.380 (4)
N1—C1	1.337 (4)	C22—N23	1.329 (4)
N1—C21	1.401 (4)	C22—H22	0.9300
N1—H1	0.74 (3)	N23—C24	1.322 (5)
C11—C12	1.367 (5)	C24—C25	1.366 (5)
C11—C16	1.409 (5)	C24—H24	0.9300
C12—C13	1.381 (5)	C25—C26	1.369 (5)
C13—C14	1.370 (6)	C25—H25	0.9300
C13—H13	0.9300	C26—H26	0.9300
C14—C15	1.369 (6)	O1W—H1W	0.75 (4)
C14—H14	0.9300	O1W—H2W	0.71 (4)
C15—C16	1.363 (5)		
C1—O2—C11	116.1 (2)	C14—C15—H15	119.2
C1—N1—C21	125.7 (3)	C15—C16—C11	117.9 (4)
C1—N1—H1	116 (2)	C15—C16—H16	121.1
C21—N1—H1	118 (2)	C11—C16—H16	121.1
O1—C1—N1	128.1 (3)	C22—C21—C26	117.5 (3)
O1—C1—O2	123.1 (3)	C22—C21—N1	117.9 (3)
N1—C1—O2	108.8 (3)	C26—C21—N1	124.6 (3)
C12—C11—O2	120.7 (3)	N23—C22—C21	124.0 (3)
C12—C11—C16	120.6 (3)	N23—C22—H22	118.0
O2—C11—C16	118.6 (3)	C21—C22—H22	118.0
C11—C12—C13	120.1 (3)	C24—N23—C22	117.2 (3)
C11—C12—Br1	118.8 (3)	N23—C24—C25	123.1 (3)
C13—C12—Br1	121.1 (3)	N23—C24—H24	118.4
C14—C13—C12	119.5 (4)	C25—C24—H24	118.4
C14—C13—H13	120.2	C24—C25—C26	119.4 (3)
C12—C13—H13	120.2	C24—C25—H25	120.3
C15—C14—C13	120.4 (4)	C26—C25—H25	120.3
C15—C14—H14	119.8	C25—C26—C21	118.8 (3)
C13—C14—H14	119.8	C25—C26—H26	120.6
C16—C15—C14	121.6 (4)	C21—C26—H26	120.6
C16—C15—H15	119.2	H1W—O1W—H2W	109 (5)
C21—N1—C1—O1	−4.6 (6)	C14—C15—C16—C11	−0.7 (5)
C21—N1—C1—O2	174.6 (3)	C12—C11—C16—C15	0.5 (5)
C11—O2—C1—O1	−10.8 (5)	O2—C11—C16—C15	176.0 (3)
C11—O2—C1—N1	169.9 (3)	C1—N1—C21—C22	157.9 (3)
C1—O2—C11—C12	−88.3 (4)	C1—N1—C21—C26	−24.6 (5)
C1—O2—C11—C16	96.3 (3)	C26—C21—C22—N23	0.1 (5)
O2—C11—C12—C13	−175.4 (3)	N1—C21—C22—N23	177.8 (3)
C16—C11—C12—C13	−0.1 (5)	C21—C22—N23—C24	0.2 (6)

O2—C11—C12—Br1	5.3 (4)	C22—N23—C24—C25	−0.2 (6)
C16—C11—C12—Br1	−179.3 (2)	N23—C24—C25—C26	−0.1 (6)
C11—C12—C13—C14	−0.3 (5)	C24—C25—C26—C21	0.4 (5)
Br1—C12—C13—C14	178.9 (3)	C22—C21—C26—C25	−0.4 (5)
C12—C13—C14—C15	0.2 (5)	N1—C21—C26—C25	−177.8 (3)
C13—C14—C15—C16	0.3 (6)		

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯O1*W*	0.74 (3)	2.10 (3)	2.832 (4)	177 (3)
O1*W*—H1*W*⋯O1[i]	0.75 (4)	2.18 (5)	2.924 (4)	177 (5)
O1*W*—H2*W*⋯N23[ii]	0.71 (4)	2.13 (4)	2.837 (4)	175 (4)
C26—H26⋯O1	0.93	2.44	2.946 (4)	114

Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) −*x*+1, −*y*+2, −*z*.