

Isomorphous crystal structures of chlorodiacetylene and iododiacetylene derivatives: simultaneous hydrogen and halogen bonds on carbonyl

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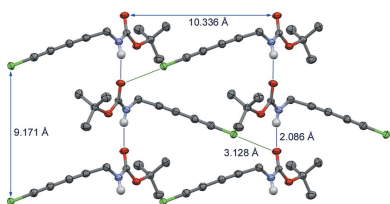
Supporting information: this article has supporting information at journals.iucr.org/e

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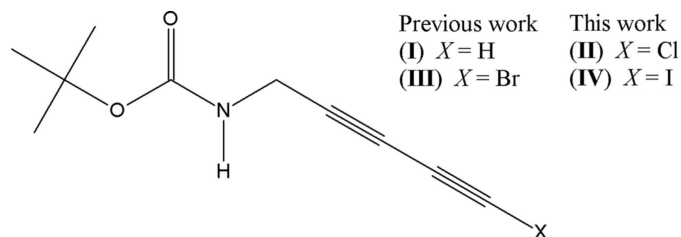
The crystal structures of *tert*-butyl (5-chloropenta-2,4-diyne-1-yl)carbamate, C₁₀H₁₂ClNO₂ (**II**), and *tert*-butyl (5-iodopenta-2,4-diyne-1-yl)carbamate, C₁₀H₁₂IINO₂ (**IV**), are isomorphous to previously reported structures and accordingly their molecular and supramolecular structures are similar. In the crystals of (**II**) and (**IV**), molecules are linked into very similar two-dimensional wall organizations with antiparallel carbamate groups involved in a combination of hydrogen and halogen bonds (bifurcated N–H···O=C and C≡C–X···O=C interactions on the same carbonyl group). There is no long-range parallel stacking of diynes, so the topochemical polymerization of diacetylene is prevented. A Cambridge Structural Database search revealed that C≡C–X···O=C contacts shorter than the sum of the van der Waals radii are scarce (only one structure for the C≡C–Cl···O=C interaction and 13 structures for the similar C≡C–I···O=C interaction).

1. Chemical context

Hydrogen bonds (HBs) and halogen bonds (XBs) are considered to be useful noncovalent synthetic tools in crystal engineering (Aakeröy *et al.*, 2015; Grabowski, 2016; Resnati *et al.*, 2015; Cinčić *et al.*, 2008). Indeed, these directional intermolecular interactions facilitate the preparation of the desired solid-state motifs and architectures (Gilday *et al.*, 2015; Cavallo *et al.*, 2016; Priimagi *et al.*, 2013; Mukherjee *et al.*, 2014; Shirman *et al.*, 2015; Mukherjee *et al.*, 2017). For example, using HBs and XBs, the specific organization of terminal diacetylenes (Li *et al.*, 2009; Ouyang *et al.*, 2003), bromodiacetylenes (Jin *et al.*, 2015) and iododiacetylenes (Jin *et al.*, 2013; Sun *et al.*, 2006) has been obtained to achieve the solid-state topochemical polymerization of diacetylenes. On the other hand, to the best of our knowledge, no chlorodiacetylene topochemical polymerizations have been reported. Our results show that chlorodiacetylene (**II**) is isostructural to iododiacetylene (**IV**) and the previously reported bromodiacetylene (**III**) and terminal diacetylene (**I**) (Baillargeon *et al.*, 2016) (see Scheme). Although the arrangement of diynes in the present article stands no chance of undergoing topochemical polymerization, we suggest that in other systems prone to polymerization, replacing Br, I or H atoms by Cl atoms in their diyne groups might result in successful PolyChloroDiAcetylene (PCDA) formation as well. This work also contributes to an emerging research theme, namely the



concept of orthogonal molecular interactions such as HBs and XBs (Kratzer *et al.*, 2015; Takemura *et al.*, 2014; Voth *et al.*, 2009), which may find applications in medicinal chemistry and chemical biology (Wilcken *et al.*, 2013).



2. Structural commentary

The molecular structures of compounds (II) and (IV) are shown in Fig. 1. All bond lengths and angles are within normal ranges. For example, the internal diyne C2–C3 bonds lengths [1.376 (3) Å for (II) and 1.385 (4) Å for (IV)] follow the useful rule of thumb describing a C–C single-bond distance (1.54 Å) decreasing by 0.04 Å each time one of the participating C atoms changes hybridization from sp^3 to sp^2 or from sp^2 to sp (Bent, 1961). Moreover, the observed distances are almost identical to those found recently in the literature for similar halodiyne (Hoheisel *et al.*, 2013; Baillargeon *et al.*, 2016). The relative orientation between the diacetylenic moiety and the carbamate functional group can be established by the absolute value of the torsion angles C4–C5–N1–C6 [111.07 (19)°] for (II) and [103.8 (3)°] for (IV).

3. Supramolecular features

In the crystals of compounds (II) and (IV), molecules are linked *via* an N–H...O=C hydrogen bond between their

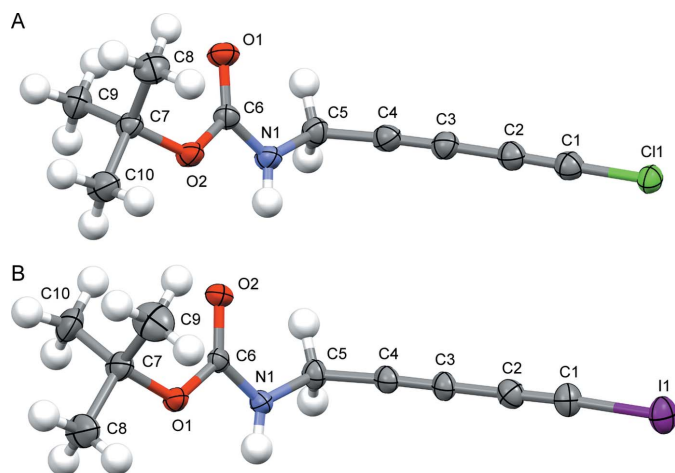


Figure 1
The molecular structure of (A) compound (II) and (B) compound (IV), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as fixed-size spheres of 0.30 Å.

Table 1
Hydrogen-bond and halogen-bond geometries (Å, °) for (II).

$D-X\cdots A$	$D-X$	$X\cdots A$	$D\cdots A$	$D-X\cdots A$
N1–H1...O1 ⁱ	0.88	2.09	2.934 (2)	162
C1–Cl1...O1 ⁱⁱ	1.665 (2)	3.127 (2)	4.792 (3)	179.01 (7)

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

respective carbamate functionalities [N1–H1...O1ⁱ (Table 1) and N1–H1...O2ⁱ (Table 2)], generating an antiparallel stacking pattern which orients the diacetylene skeleton on each side of the one-dimensional carbamate tape (parts B and D in Fig. 2). For both crystals, the simultaneous presence of halogen and hydrogen bonds with the carbamate O atom have been found. Indeed, additional halogen-bond interactions

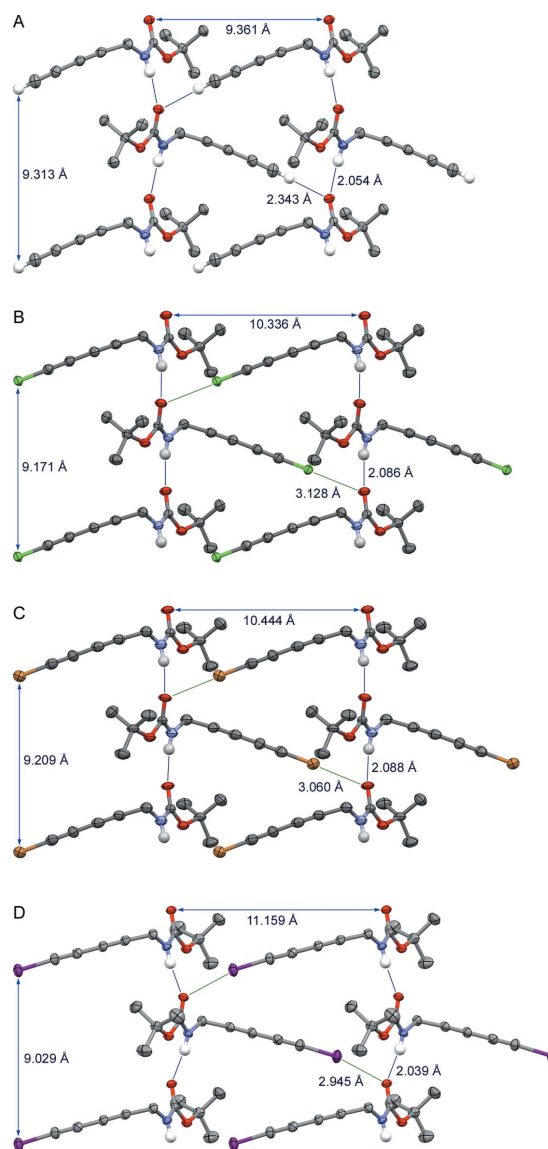


Figure 2
Halogen (green lines) and/or hydrogen bonds (blue lines) inside the supramolecular walls of (A) diyne (II), (B) chlorodiyne (II), (C) bromodiyne (III) and (D) iododiyne (IV). The nonpolar H atoms have been omitted for clarity.

Table 2
Hydrogen-bond and halogen-bond geometries (Å, °) for (**IV**).

$D-X\cdots A$	$D-X$	$X\cdots A$	$D\cdots A$	$D-X\cdots A$
$N1-H1\cdots O2^i$	0.88	2.04	2.881 (2)	160
$C1-I1\cdots O2^{ii}$	1.999 (2)	2.945 (2)	4.919 (3)	168.31 (8)

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

occur with the carbamate O atom [$Cl1\cdots O1^{ii}$ for (**II**) and $I1\cdots O2^{ii}$ for (**IV**)], resulting in an infinite two-dimensional network that can be considered as polar supramolecular walls. This arrangement is similar to our previous work (Baillargeon *et al.*, 2016) on the terminal diacetylene (**I**) (part A in Fig. 2) and the bromodiacetylene (**III**) (part C in Fig. 2). In fact, diynes (**I**)–(**IV**) (Fig. 2) constitute a complete set of truly isomorphous crystals that can be carefully examined to evaluate the differences and similarities that exist between halogen and hydrogen bonds. Thus, the $X\cdots O\cdots H$ angle increases as the size of the halogen atom becomes larger. This angle, which is pretty open in the chlorine crystal (**II**) ($Cl1\cdots O1\cdots H1$; part B in Fig. 2; 69°) adopts a near orthogonal geometry with the iodine ($I1\cdots O2\cdots H1$; part D in Fig. 2; 83°). It is not a surprise that the bromine crystal (**III**) represents an intermediate case (part C in Fig. 2; 72°). The value for the terminal diacetylene (**I**) $X = H$ (part A in Fig. 2; 76°) is closely related to the bromodiacetylene (Baillargeon *et al.*, 2016).

4. Database survey

A survey of the Cambridge Structural Database (*Conquest* Version 1.19; CSD, Version 5.38, November 2016 plus 3 updates; Groom *et al.*, 2016) furnished 404 hits of terminal alkynes $CC-H$ having close contacts with carbonyl $O=C$ (shorter than the sum of their van der Waals radii). On the other hand, similar contacts from halogenoalkyne analogs are scarce (1 hit for the chloroalkyne, 4 hits for the bromoalkyne

and 13 hits for the iodoalkyne; Table 3). For the iodoalkyne, results are limited to monovalent iodine and for a structure in which the carbonyl group is not involved in an organometallic complex.

5. Synthesis and crystallization

5.1. Compound (II)

Tetra-*n*-butylammonium fluoride (TBAF, 0.437 ml, 1 M in THF, 0.437 mmol), $AgNO_3$ (39 mg, 0.23 mmol) and NCS (190 mg, 1.42 mmol) were added to a solution of $BocNHCH_2-C\equiv C-C\equiv C-TMS$ (183 mg, 0.728 mmol) in acetonitrile (3 ml) at room temperature. The resulting mixture was stirred for 2.5 h under N_2 in the absence of light. Purification of the crude product by flash chromatography on silica gel, eluting with mixtures of Hex/DCM/ Et_2O (gradient from 9:1:1 to 1:1:1), provided compound (**II**) as a beige solid (yield 72 mg, 46%). Single crystals suitable for X-ray diffraction were prepared by diffusion of pentane into a chloroform solution of (**II**) at 263 K. $R_F = 0.43$ (2:1:1 Hex/DCM/ Et_2O); IR (UATR, ν , cm^{-1}): 3326, 2977, 2920, 2255, 2168, 1673, 1531, 1421, 1368, 1278, 1248, 1222, 1158, 1143, 1042, 1028, 933, 849, 761, 718, 655; 1H NMR (400 MHz, $CDCl_3$): δ 4.72 (*br*, 1H), 3.99 (*d*, 2H), 1.45 (*s*, 9H); HRMS (m/z): calculated for $C_{10}H_{12}CINNaO_2 [MNa^+]$: 236.0449, found: 236.0448.

5.2. Compound (IV)

TBAF (0.437 ml, 1 M in THF, 0.437 mmol), $AgNO_3$ (39 mg, 0.23 mmol) and NIS (328 mg, 1.46 mmol) were added to a solution of $BocNHCH_2-C\equiv C-C\equiv C-TMS$ (183 mg, 0.728 mmol) in acetonitrile (3 ml) at room temperature. The resulting mixture was stirred for 2.5 h under N_2 in the absence of light. Purification of the crude product by flash chromatography on silica gel, eluting with mixtures of Hex/DCM/ Et_2O (gradient from 9:1:1 to 1:1:1) provided compound (**IV**) as a beige solid (yield 95 mg, 43%). Single crystals suitable for

Table 3
CSD data (Groom *et al.*, 2016) retrieved for the $C\equiv C-X\cdots O=C$ contacts shorter than the sum of their van der Waals radii.

$C\equiv C-X\cdots O=C$ contacts	CSD refcode	Space group	$X\cdots O$ distance (Å)	$C-X\cdots O$ angle (°)	Reference
$C\equiv C-Cl\cdots O=C$	NIDWAA	$P\bar{1}$	3.111; 3.241	152.59; 158.76	Kawai <i>et al.</i> (2013)
$C\equiv C-Br\cdots O=C$	HEVWAI	$C2$	2.959	158.12	Hoheisel <i>et al.</i> (2013)
$C\equiv C-Br\cdots O=C$	HEVWAI01	$P2_12_12_1$	2.966	166.70	Hoheisel <i>et al.</i> (2013)
$C\equiv C-Br\cdots O=C$	NIDWII	$P2_1/n$	2.867	171.11	Kawai <i>et al.</i> (2013)
$C\equiv C-Br\cdots O=C$	KAMXII	$P2_1/c$	3.060	178.26	Baillargeon <i>et al.</i> (2016)
$C\equiv C-I\cdots O=C$	COHYUU	$P\bar{1}$	3.096	164.55	Luo <i>et al.</i> (2008)
$C\equiv C-I\cdots O=C$	IYAYUC	$Pca2_1$	2.861	170.36	Hou <i>et al.</i> (2004)
$C\equiv C-I\cdots O=C$	MASVUZ	$P2_1/n$	2.834; 2.887	170.72; 172.97	Perkins <i>et al.</i> (2012)
$C\equiv C-I\cdots O=C$	TOYPUS	$P2_1/c$	2.933	175.36	Avtomonov <i>et al.</i> (1997)
$C\equiv C-I\cdots O=C$	HOWXIC	$P2_1/c$	2.887	169.51	Dumele <i>et al.</i> (2014)
$C\equiv C-I\cdots O=C$	LUNKOW	$P2/c$	2.791	174.12	Kratzer <i>et al.</i> (2015)
$C\equiv C-I\cdots O=C$	LUNKUC	$P2_1/c$	2.754	172.63	Kratzer <i>et al.</i> (2015)
$C\equiv C-I\cdots O=C$	LUNLAJ	$P2_1/c$	2.773	173.70	Kratzer <i>et al.</i> (2015)
$C\equiv C-I\cdots O=C$	LUNLIR	$Pca2_1$	2.858	170.94	Kratzer <i>et al.</i> (2015)
$C\equiv C-I\cdots O=C$	LUNLOX	$C2/c$	2.763	175.58	Kratzer <i>et al.</i> (2015)
$C\equiv C-I\cdots O=C$	IBUYAI	$P2_1/m$	2.856	177.96	Dumele <i>et al.</i> (2017)
$C\equiv C-I\cdots O=C$	IBUYOW	$P2_1/c$	2.830	176.52	Dumele <i>et al.</i> (2017)
$C\equiv C-I\cdots O=C$	IBUYUC	$P\bar{1}$	2.878	177.89	Dumele <i>et al.</i> (2017)

Table 4
Experimental details.

	(II)	(IV)
Crystal data		
Chemical formula	C ₁₀ H ₁₂ ClNO ₂	C ₁₀ H ₁₂ INO ₂
<i>M_r</i>	213.66	305.11
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	173	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.336 (3), 9.171 (3), 11.870 (3)	11.1587 (16), 9.0288 (13), 12.9899 (18)
β (°)	100.656 (5)	108.731 (2)
<i>V</i> (Å ³)	1105.8 (5)	1239.4 (3)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.32	2.56
Crystal size (mm)	0.34 × 0.22 × 0.02	0.36 × 0.3 × 0.28
Data collection		
Diffractometer	Bruker APEXII	Bruker APEXII
Absorption correction	Multi-scan (SADABS; Bruker, 2008)	Multi-scan (SADABS; Bruker, 2008)
<i>T</i> _{min} , <i>T</i> _{max}	0.66, 0.745	0.675, 0.745
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	16132, 2249, 1755	17970, 2532, 2342
<i>R</i> _{int}	0.045	0.02
(sin θ/λ) _{max} (Å ⁻¹)	0.625	0.626
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.089, 1.06	0.022, 0.054, 1.08
No. of reflections	2249	2532
No. of parameters	130	130
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.22, -0.21	1.32, -0.69

Computer programs: APEX2 (Bruker, 2008), SAINT (Bruker, 2008), SORTAV (Blessing, 1995), SHELXS97 (Sheldrick, 2008), SHELXL2016 (Sheldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012), Mercury (Macrae et al., 2006), WinGX (Farrugia, 2012) and publCIF (Westrip, 2010).

X-ray diffraction were prepared by slow evaporation from a chloroform solution of (IV) at room temperature. *R*_F = 0.48 (2:1:1 Hex/DCM/Et₂O); IR (UATR, ν, cm⁻¹): 3328, 2980, 2933, 2230, 2159, 1661, 1532, 1451, 1420, 1367, 1284, 1250, 1154, 1142, 1042, 1026, 929, 851, 762, 714, 647; ¹H NMR (400 MHz, CDCl₃): δ 4.73 (*br*, 1H), 4.02 (*d*, 2H), 1.44 (*s*, 9H).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4.

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supporting information

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Computing details

For both structures, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *pubCIF* (Westrip, 2010).

tert-Butyl (5-chloropenta-2,4-diyne-1-yl)carbamate (II)

Crystal data

C₁₀H₁₂ClNO₂

M_r = 213.66

Monoclinic, *P2₁/c*

Hall symbol: -P 2ybc

a = 10.336 (3) Å

b = 9.171 (3) Å

c = 11.870 (3) Å

β = 100.656 (5)°

V = 1105.8 (5) Å³

Z = 4

F(000) = 448

D_x = 1.283 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 8841 reflections

θ = 2.8–26.4°

μ = 0.32 mm⁻¹

T = 173 K

Plate, orange

0.34 × 0.22 × 0.02 mm

Data collection

Bruker APEXII
diffractometer

Radiation source: sealed x-ray tube

Graphite monochromator

φ or ω oscillation scans

Absorption correction: multi-scan
(SADABS; Bruker, 2008)

T_{min} = 0.66, *T_{max}* = 0.745

16132 measured reflections

2249 independent reflections

1755 reflections with *I* > 2σ(*I*)

R_{int} = 0.045

θ_{\max} = 26.4°, θ_{\min} = 2.0°

h = -12→12

k = -11→11

l = -9→14

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.036

wR(*F*²) = 0.089

S = 1.06

2249 reflections

130 parameters

0 restraints

0 constraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.2863P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.40035 (19)	0.0211 (2)	0.15762 (16)	0.0343 (4)
C2	0.50716 (18)	-0.0266 (2)	0.15615 (16)	0.0336 (4)
C3	0.63096 (19)	-0.0798 (2)	0.15309 (16)	0.0336 (4)
C4	0.73990 (19)	-0.1223 (2)	0.15037 (16)	0.0334 (4)
C5	0.87519 (17)	-0.1687 (2)	0.14761 (17)	0.0339 (4)
H5A	0.882935	-0.274828	0.16243	0.041*
H5B	0.894345	-0.150569	0.070125	0.041*
C6	1.04144 (17)	-0.15939 (19)	0.32333 (15)	0.0271 (4)
C7	1.22986 (18)	-0.11065 (19)	0.47967 (15)	0.0304 (4)
C8	1.1748 (2)	-0.1841 (2)	0.57483 (17)	0.0439 (5)
H8A	1.106364	-0.122368	0.597047	0.066*
H8B	1.245644	-0.198955	0.641132	0.066*
H8C	1.136913	-0.278618	0.547923	0.066*
C9	1.32333 (19)	-0.2075 (2)	0.42986 (18)	0.0408 (5)
H9A	1.278745	-0.298815	0.40299	0.061*
H9B	1.400577	-0.228971	0.488902	0.061*
H9C	1.351283	-0.15766	0.365371	0.061*
C10	1.2953 (2)	0.0332 (2)	0.52078 (19)	0.0449 (5)
H10A	1.324136	0.082715	0.456527	0.067*
H10B	1.371735	0.014414	0.581378	0.067*
H10C	1.232365	0.095115	0.550916	0.067*
C11	0.24981 (4)	0.08590 (5)	0.15756 (4)	0.03061 (14)
N1	0.97160 (14)	-0.09282 (16)	0.23144 (13)	0.0314 (4)
H1	0.984766	0.000739	0.221551	0.038*
O1	1.03225 (13)	-0.28874 (13)	0.34594 (11)	0.0361 (3)
O2	1.12149 (12)	-0.06256 (12)	0.38708 (11)	0.0311 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0342 (11)	0.0349 (11)	0.0334 (11)	-0.0009 (9)	0.0055 (8)	0.0009 (8)
C2	0.0337 (11)	0.0333 (10)	0.0323 (11)	-0.0036 (8)	0.0019 (8)	0.0007 (8)
C3	0.0333 (11)	0.0300 (10)	0.0346 (11)	-0.0005 (8)	-0.0011 (8)	0.0016 (8)
C4	0.0339 (11)	0.0279 (10)	0.0350 (11)	-0.0023 (8)	-0.0028 (8)	-0.0006 (8)
C5	0.0309 (10)	0.0311 (10)	0.0368 (11)	0.0013 (8)	-0.0014 (8)	-0.0030 (8)
C6	0.0264 (9)	0.0222 (9)	0.0323 (10)	-0.0014 (7)	0.0045 (7)	-0.0023 (7)

C7	0.0311 (10)	0.0269 (10)	0.0299 (10)	0.0017 (8)	-0.0026 (8)	0.0021 (8)
C8	0.0524 (13)	0.0429 (12)	0.0369 (12)	0.0014 (10)	0.0091 (10)	0.0049 (9)
C9	0.0344 (11)	0.0415 (12)	0.0451 (13)	0.0056 (9)	0.0037 (9)	0.0019 (9)
C10	0.0468 (13)	0.0339 (11)	0.0462 (13)	-0.0041 (10)	-0.0121 (10)	-0.0007 (9)
C11	0.0268 (2)	0.0320 (3)	0.0337 (3)	0.00451 (19)	0.00733 (18)	0.00090 (19)
N1	0.0303 (8)	0.0220 (8)	0.0381 (9)	-0.0024 (7)	-0.0036 (7)	0.0013 (7)
O1	0.0409 (8)	0.0217 (7)	0.0427 (8)	-0.0034 (6)	0.0003 (6)	0.0014 (6)
O2	0.0314 (7)	0.0220 (7)	0.0358 (8)	-0.0009 (5)	-0.0049 (6)	-0.0006 (5)

Geometric parameters (Å, °)

C1—C2	1.191 (3)	C6—N1	1.339 (2)
C1—C11	1.666 (2)	C6—O2	1.347 (2)
C2—C3	1.376 (3)	C7—O2	1.484 (2)
C3—C4	1.198 (3)	C7—C9	1.511 (3)
C4—C5	1.468 (3)	C7—C8	1.513 (3)
C5—N1	1.449 (2)	C7—C10	1.521 (3)
C6—O1	1.224 (2)		
C2—C1—C11	178.9 (2)	O2—C7—C9	109.55 (15)
C1—C2—C3	179.0 (2)	O2—C7—C8	110.41 (15)
C4—C3—C2	178.2 (2)	C9—C7—C8	112.70 (16)
C3—C4—C5	177.8 (2)	O2—C7—C10	102.12 (14)
N1—C5—C4	112.49 (16)	C9—C7—C10	110.89 (17)
O1—C6—N1	124.66 (17)	C8—C7—C10	110.67 (17)
O1—C6—O2	125.48 (17)	C6—N1—C5	122.64 (16)
N1—C6—O2	109.86 (15)	C6—O2—C7	121.42 (13)
O1—C6—N1—C5	0.3 (3)	N1—C6—O2—C7	-166.78 (14)
O2—C6—N1—C5	-178.98 (15)	C9—C7—O2—C6	59.3 (2)
C4—C5—N1—C6	111.1 (2)	C8—C7—O2—C6	-65.4 (2)
O1—C6—O2—C7	13.9 (3)	C10—C7—O2—C6	176.85 (16)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1 ⁱ	0.88	2.09	2.935	162
C1—C11...O1 ⁱⁱ	1.67	3.13	4.793	179

Symmetry codes: (i) $-x+2, y+1/2, -z+1/2$; (ii) $-x+1, y+1/2, -z+1/2$.***tert*-Butyl (5-iodopenta-2,4-diyne-1-yl)carbamate (IV)***Crystal data*

C₁₀H₁₂INO₂
M_r = 305.11
 Monoclinic, *P*2₁/*n*
 Hall symbol: -*P* 2₁*y**n*
a = 11.1587 (16) Å
b = 9.0288 (13) Å

c = 12.9899 (18) Å
 β = 108.731 (2)°
V = 1239.4 (3) Å³
Z = 4
F(000) = 592
D_x = 1.635 Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 9940 reflections
 $\theta = 2.3\text{--}26.4^\circ$
 $\mu = 2.56 \text{ mm}^{-1}$

$T = 173 \text{ K}$
 Prism, yellow
 $0.36 \times 0.3 \times 0.28 \text{ mm}$

Data collection

Bruker APEXII
 diffractometer
 Radiation source: sealed x-ray tube
 Graphite monochromator
 φ or ω oscillation scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2008)
 $T_{\min} = 0.675$, $T_{\max} = 0.745$

17970 measured reflections
 2532 independent reflections
 2342 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.02$
 $\theta_{\max} = 26.4^\circ$, $\theta_{\min} = 2.1^\circ$
 $h = -12 \rightarrow 13$
 $k = -11 \rightarrow 11$
 $l = -15 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.054$
 $S = 1.08$
 2532 reflections
 130 parameters
 0 restraints
 0 constraints

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 1.7447P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.69 \text{ e \AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2157 (2)	1.0340 (3)	0.3437 (2)	0.0328 (6)
C2	0.3210 (2)	1.0012 (3)	0.34873 (19)	0.0304 (5)
C3	0.4425 (2)	0.9623 (3)	0.35280 (19)	0.0279 (5)
C4	0.5465 (2)	0.9286 (3)	0.35525 (19)	0.0275 (5)
C5	0.6760 (2)	0.8938 (3)	0.35692 (19)	0.0282 (5)
H5A	0.736704	0.927089	0.42691	0.034*
H5B	0.684833	0.785076	0.352172	0.034*
C6	0.7111 (2)	0.8882 (2)	0.18051 (19)	0.0219 (4)
C7	0.7579 (3)	0.9226 (3)	0.0094 (2)	0.0344 (6)
C8	0.7976 (4)	1.0622 (3)	-0.0367 (3)	0.0511 (8)
H8A	0.730469	1.136625	-0.049832	0.077*
H8B	0.812386	1.038609	-0.105307	0.077*
H8C	0.875616	1.101212	0.015278	0.077*
C9	0.6338 (4)	0.8624 (4)	-0.0654 (3)	0.0559 (9)
H9A	0.611252	0.772368	-0.033698	0.084*
H9B	0.642508	0.839113	-0.136337	0.084*
H9C	0.567195	0.936832	-0.074587	0.084*

C10	0.8637 (3)	0.8100 (4)	0.0377 (3)	0.0506 (8)
H10A	0.936443	0.849222	0.095807	0.076*
H10B	0.888703	0.789497	-0.02666	0.076*
H10C	0.834626	0.718248	0.062297	0.076*
N1	0.7077 (2)	0.9636 (2)	0.26832 (16)	0.0263 (4)
H1	0.725256	1.058913	0.272455	0.032*
O1	0.73962 (17)	0.97953 (18)	0.11063 (13)	0.0272 (4)
O2	0.69111 (17)	0.75519 (18)	0.16743 (14)	0.0289 (4)
I1	0.04221 (2)	1.09875 (2)	0.33737 (2)	0.03907 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0294 (14)	0.0398 (14)	0.0301 (13)	0.0020 (11)	0.0106 (10)	0.0027 (11)
C2	0.0333 (14)	0.0328 (13)	0.0263 (12)	-0.0012 (11)	0.0110 (10)	0.0031 (10)
C3	0.0312 (14)	0.0309 (13)	0.0250 (11)	-0.0015 (10)	0.0139 (10)	0.0011 (10)
C4	0.0337 (14)	0.0284 (12)	0.0236 (11)	-0.0036 (10)	0.0135 (10)	0.0005 (9)
C5	0.0298 (13)	0.0321 (13)	0.0259 (12)	0.0007 (10)	0.0132 (10)	0.0032 (10)
C6	0.0180 (11)	0.0216 (11)	0.0271 (11)	0.0013 (8)	0.0087 (9)	0.0020 (9)
C7	0.0490 (17)	0.0323 (13)	0.0293 (13)	-0.0017 (12)	0.0229 (12)	-0.0034 (10)
C8	0.085 (3)	0.0407 (17)	0.0437 (17)	-0.0055 (16)	0.0430 (18)	0.0016 (13)
C9	0.067 (2)	0.065 (2)	0.0325 (15)	-0.0141 (18)	0.0106 (15)	-0.0046 (15)
C10	0.065 (2)	0.0415 (17)	0.063 (2)	0.0074 (15)	0.0446 (18)	-0.0051 (15)
N1	0.0334 (11)	0.0215 (10)	0.0304 (10)	-0.0039 (8)	0.0191 (9)	-0.0015 (8)
O1	0.0396 (10)	0.0196 (8)	0.0293 (9)	0.0004 (7)	0.0209 (7)	0.0004 (7)
O2	0.0348 (10)	0.0197 (8)	0.0352 (9)	-0.0030 (7)	0.0157 (8)	-0.0001 (7)
I1	0.02499 (10)	0.04928 (12)	0.04157 (11)	0.00657 (8)	0.00878 (7)	0.00614 (8)

Geometric parameters (Å, °)

C1—C2	1.193 (4)	C7—C9	1.514 (4)
C1—I1	1.999 (3)	C7—C8	1.521 (4)
C2—C3	1.385 (4)	C8—H8A	0.98
C3—C4	1.191 (4)	C8—H8B	0.98
C4—C5	1.472 (3)	C8—H8C	0.98
C5—N1	1.452 (3)	C9—H9A	0.98
C5—H5A	0.99	C9—H9B	0.98
C5—H5B	0.99	C9—H9C	0.98
C6—O2	1.223 (3)	C10—H10A	0.98
C6—O1	1.338 (3)	C10—H10B	0.98
C6—N1	1.340 (3)	C10—H10C	0.98
C7—O1	1.486 (3)	N1—H1	0.88
C7—C10	1.512 (4)		
C2—C1—I1	177.3 (3)	H8A—C8—H8B	109.5
C1—C2—C3	179.1 (3)	C7—C8—H8C	109.5
C4—C3—C2	179.4 (3)	H8A—C8—H8C	109.5
C3—C4—C5	177.4 (3)	H8B—C8—H8C	109.5

N1—C5—C4	112.5 (2)	C7—C9—H9A	109.5
N1—C5—H5A	109.1	C7—C9—H9B	109.5
C4—C5—H5A	109.1	H9A—C9—H9B	109.5
N1—C5—H5B	109.1	C7—C9—H9C	109.5
C4—C5—H5B	109.1	H9A—C9—H9C	109.5
H5A—C5—H5B	107.8	H9B—C9—H9C	109.5
O2—C6—O1	125.7 (2)	C7—C10—H10A	109.5
O2—C6—N1	124.3 (2)	C7—C10—H10B	109.5
O1—C6—N1	110.00 (19)	H10A—C10—H10B	109.5
O1—C7—C10	109.6 (2)	C7—C10—H10C	109.5
O1—C7—C9	109.6 (2)	H10A—C10—H10C	109.5
C10—C7—C9	113.4 (3)	H10B—C10—H10C	109.5
O1—C7—C8	101.7 (2)	C6—N1—C5	122.3 (2)
C10—C7—C8	110.5 (3)	C6—N1—H1	118.8
C9—C7—C8	111.5 (3)	C5—N1—H1	118.8
C7—C8—H8A	109.5	C6—O1—C7	121.17 (18)
C7—C8—H8B	109.5		
O2—C6—N1—C5	-1.7 (4)	N1—C6—O1—C7	175.9 (2)
O1—C6—N1—C5	178.5 (2)	C10—C7—O1—C6	-58.9 (3)
C4—C5—N1—C6	-103.9 (3)	C9—C7—O1—C6	66.1 (3)
O2—C6—O1—C7	-3.9 (4)	C8—C7—O1—C6	-175.8 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O2 ⁱ	0.88	2.04	2.881	160
C1—H1...O2 ⁱⁱ	2.00	2.95	4.919	168

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